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REACTION OF IODINE CHLORIDE AND IODINE TRICHLORIDE WITH HYPOPHOSPHOROUS ACID

Ya. A. Fialkov and F. E. Kagan

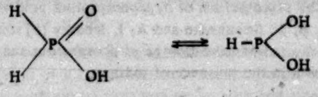
As is well known, hypophosphorous acid can be classified as a fairly strong reducing agent.

On the basis of the study of the oxidation reactions of hypophosphorous acid with various oxidizing agents, methods have been developed for the quantitative determination of hypophosphorous acid and its salts by the use of bromine [1], iodine [2], and potassium permanganate [3].

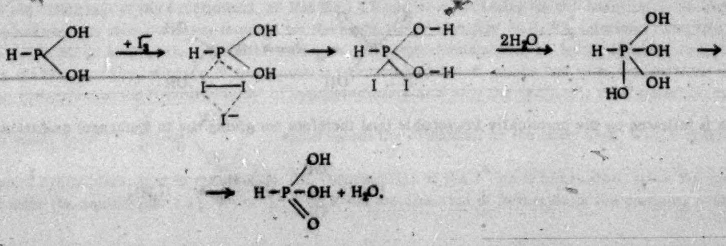
In the study of the oxidation mechanism of hypophosphorous acid attention has been directed to the unusual kinetics of its oxidation, namely, that at low oxidant concentration, the rate of oxidation of hypophosphorous acid by means of halogens, mercuric chloride and silver nitrate does not depend on the nature and the concentration of the oxidizing agent, but only on the proportional concentration of hydrogen ions [6].

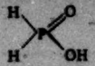
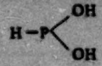
The rate of oxidation of H_3PO_2 into H_3PO_3 is very low in alkaline medium but increases in proportion to the acidity of the solution. Hypophosphorous acid is an acid of medium strength. Its dissociation constant is equal to $9 \cdot 10^{-2}$. Addition of a strong acid (hydrochloric and so forth) suppresses the dissociation of hypophosphorous acid. Consequently, undissociated H_3PO_2 is oxidized faster than its ions.

The unusual behavior of hypophosphorous acid as a reducing agent can be explained by the peculiarity of its structure. E. I. Orlov [4], in a study of the kinetics of the oxidation of H_3PO_2 with iodine, came to the conclusion that in a solution of hypophosphorous acid there is a tautomeric equilibrium of the two forms:



In the opinion of Orlov, the oxidation reaction with iodine proceeds by way of preliminary addition of iodine to "the unsaturated form of hypophosphorous acid $HP(OH)_2$ at the latent valencies"; as a result of the reaction the addition product of iodine to H_3PO_2 forms phosphorous acid with water which Orlov depicts in the following fashion:



Since the oxidation with iodine proceeds only in acid medium and the presence of alkali prevents the reaction, the author concluded that the acidic medium favors the transition  to , and that this makes possible the reaction with iodine. The existence of two tautomeric forms of hypophosphorous acid has also been suggested by other investigators. Stell [5] studied the oxidation of hypophosphorous acid with iodine at low concentration of the oxidizing agent. To explain the fact that the rate of oxidation of H_3PO_2 did not depend on the concentration of oxidizing agent, he assumed that the oxidation of hypophosphorous acid into phosphorous, $H_2PO_2^- + I_2 + H_2O = HPO_3^{--} + 3H^+ + 2I^-$, proceeds by the two following reactions:

$$H_2PO_2^- + H_2O = HPO_3^{--} + 3H^+ + 2e,$$

$$2H^+ + I_2 + 2e = 2H^+ + 2I^- .$$

The rate of the first of these reactions is very low in comparison with the rate with which iodine molecules can be converted into ions, as a consequence of which, in the opinion of the author, the rate of the whole reaction does not depend on the iodine concentration.

Mitchell [6] assumed that in acidic medium the hypophosphorous acid molecules are not ionized and are found in equilibrium with a small quantity of "active" molecules of H_5PO_3,

$$H_3PO_2 + H_2O \rightleftharpoons H_5PO_3,$$

which rapidly react with iodine:

$$H_5PO_3 + I_3^- \rightarrow H_3PO_3 + 2H^+ + 3I^-$$

Thus, the equilibrium is displaced and the rate of the reaction $H_3PO_2 + H_2O \rightleftharpoons H_5PO_3$ becomes measurable. However, Mitchell did not explain why H_5PO_3 should be an active form of hypophosphorous acid.

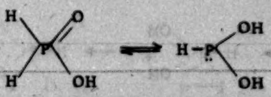
Thus, on the basis of the literature data one may conclude that in the oxidation of hypophosphorous acid, the transition of "inactive" forms into "active" has great significance and that this reaction is catalyzed by hydrogen ions.

The oxidation with iodine can, consequently, be represented by the scheme:

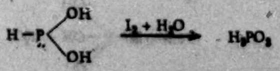
$$\underset{\text{inactive}}{H_3PO_2} \rightleftharpoons \underset{\text{active}}{H_3PO_2} \xrightarrow{I_2 + H_2O} H_3PO_3.$$

The assumption concerning the tautomerism of hypophosphorous acid was confirmed by Brodsky and his coworkers [7, 8]. L. I. Chervyatsova, D. N. Strazhesko and A. I. Brodsky [7] studied the isotopic exchange of phosphorous between H_3PO_2 containing the radioactive isotope of phosphorous and H_3PO_3 and showed that there was no isotopic exchange between them even in the presence of iodine.

The absence of isotopic exchange can serve as a new argument in favor of the existence of tautomerism of hypophosphorous acid: this fact can explain why the oxidation proceeds in two stages: a reversible (but not leading to exchange) tautomeric conversion into the active form with a coordination-unsaturated atom of phosphorous:



which is followed by the practically irreversible (and therefore not giving rise to exchange) oxidation:



A. I. Brodsky and L. V. Sulima [8], in a study of the isotopic exchange reaction of hypophosphoric acid and its sodium salt with heavy water, obtained conclusive evidence of the existence of tautomerism in hypophosphorous acid and of its absence in the anion of this acid. This work confirmed the scheme for the tautomeric conversion of H_3PO_2 set forth above.

Directing our attention to the work of Orlov [4] and the investigations of A. I. Brodsky and his coworkers [7, 8], we decided to take electropositive iodine compounds – ICl and ICl_3 as oxidizing agents for H_3PO_2, assuming that the study of these reactions would confirm the ideas of E. I. Orlov concerning the mechanism of oxidation of hypophosphorous acid by iodine solution. At the same time we aimed to develop a method for the quantitative determination of H_3PO_2 and its salts based on the use of these oxidizing agents.

EXPERIMENTAL

$NaH_2PO_2 \cdot H_2O$ and hydrochloric acid solutions of ICl and ICl_3 in which the latter was contained in the form of the complex acids $HICl_2$ and $HICl_4$ found in equilibrium with the products of their electrolytic dissociation, were taken for the experiments. These solutions were prepared from KI and KIO_3, taken in stochiometric quantities, and hydrochloric acid, calculated to obtain 0.1 N solution of ICl and ICl_3 in 0.4 N HCl solution [9, 10]. For one of the series of experiments 0.1 N solution of $NaICl_4$ was obtained from crystalline ICl_3 and an aqueous solution of sodium chloride.

Preliminary experiments showed that the reaction of hypophosphorous acid with iodine chloride proceeded with the evolution of iodine. This gave a basis for assuming that the process of oxidation can be expressed by the following equations:

$$H_3PO_2 + 4ICl + 2H_2O = H_3PO_4 + 2I_2 + 4HCl, \qquad (1)$$

$$NaH_2PO_2 + 4ICl + 2H_2O = NaCl + H_3PO_4 + 2I_2 + 3HCl. \qquad (2)$$

In order to confirm this hypothesis, we dissolved a batch of sodium hypophosphite in 2-3 ml of 8% HCl, shook it with excess 0.1 N hydrochloric acid solution of iodine chloride, and after several hours extracted the iodine that separated with chloroform; the chloroform extract was titrated with 0.1 N sodium thiosulfate solution. 3.99 and 4.02 g-atoms of iodine were evolved per 1 mole of $NaH_2PO_2 \cdot H_2O$.

These experiments showed that hypophosphorous acid and its sodium salt are quantitatively oxidized by iodine chloride, in agreement with equation (1) or (2). The g-equivalents of H_3PO_2 and $NaH_2PO_2 \cdot H_2O$ were equal to 0.25 g-molecular weight.

For a more detailed study of this reaction, it was necessary to establish the minimum time necessary for complete oxidation of the hypophosphorous acid into phosphoric acid with iodine chloride and also the influence of the hydrogen ion concentration on the oxidation process. According to the literature data [4], acid catalyzes the oxidation reaction of hypophosphorous acid with iodine.

For elucidating these questions, the following experiments were set up: to 5 ml of approximately 0.1 N $NaH_2PO_2 \cdot H_2O$ solution was added 25 ml of 0.1 N ICl solution and then after various intervals of time, the iodine which separated was extracted. The same experiment was set up with addition of various quantities of hydrochloric acid to the reaction mixture. The results of these experiments are set forth in Table 1.

As is evident from the data of Table 1, addition of hydrochloric acid slows the oxidation reaction of sodium hypophosphite solutions (or of solutions of hypophosphorous acid).

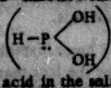
Under the conditions of the experiments, no less than 4 hours were necessary for the quantitative oxidation of sodium hypophosphite; more time was required for the oxidation of acidified NaH_2PO_2 solutions. The retarding influence of hydrochloric acid on the rate of the oxidation of hypophosphorous acid by iodine chloride can be explained by the fact that the influence of two factors is superimposed here: on the one hand, hydrochloric acid catalyzes the conversion of the "inactive form" of hypophosphorous acid into the "active", unsaturated as regards coordination bonds, form  $\left(H-\ddot{P}\begin{matrix}OH\\OH\end{matrix}\right)$, which speeds the oxidation; on the other hand, with increasing concentration of hydrochloric acid in the solution, the concentration of the I^+ ion is diminished, since the hydrochloric acid shifts the equilibrium $ICl_2^- \rightleftharpoons I^+ + 2Cl^-$ in the direction of formation of the complex acid $H[ICl_2]$.

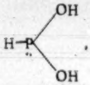
TABLE 1

The influence of duration of the reaction and concentration of hydrochloric acid on the rate of oxidation of $NaH_2PO_2 \cdot H_2O$

Duration of the reaction (in hours)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$ (%)		
	Without addition of HCl	5 ml of 1 N HCl solution added	10 ml of 1 N HCl solution added
0.5	51.24	—	35.10
1	79.47	54.75	53.90
3	97.90	89.48	77.20
4	99.80	92.48	85.29
5	—	98.97	89.48
6	—	—	95.43

Since the oxidation of hypophosphorous acid with iodine chloride evidently proceeds via addition to the free electron pair of the phosphorous in $H-\ddot{P}(OH)_2$ of electropositive iodine, which acts as an electron acceptor, in the end the increased concentration of hydrochloric acid, associated with the diminished concentration of I^+ ions in the solution, lowers the rate of oxidation of hypophosphorous acid by iodine chloride.

The influence of the concentration of hydrochloric acid on the rate of oxidation of hypophosphorous acid by iodine chloride confirms the opinion concerning the existence of coordination-unsaturated forms of hypophosphorous acid



$H-\ddot{P}(OH)_2$

, and also confirms the opinion expressed by Orlov, that the oxidation of hypophosphorous acid by iodine proceeds by way of preliminary addition of iodine to H_3PO_2.

Further investigations of the oxidative capacity of iodine halides in neutral medium reinforced our explanation of the influence of the concentration of acid on the rate of oxidation of hypophosphorous acid by iodine halides. Experiments were conducted with a solution of $NaICl_4$ (see above) in neutral medium, and also with the addition of various quantities of hydrochloric acid. The results of the determinations are set forth in Table 2.

TABLE 2

Influence of the acid concentration on the rate of oxidation of $NaH_2PO_2 \cdot H_2O$ by ICl_3 in NaCl. Weighed portions of $NaH_2PO_2 \cdot H_2O$ of 0.2600 g in 100 ml of water. For a single determination: 5 ml of solution and 25 ml of 0.1 N solution of $NaICl_4$. Temperature 60-70°

Experiment Number	Duration of reaction	Amount of 1 N HCl solution added (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
			(in g)	(in %)
1	60 minutes	—	0.2088	80.3
2	120 minutes	—	0.2104	80.9
3	42 hours	—	0.2597	99.9
4	60 minutes	1	0.2258	86.9
5	60 minutes	5	0.2597	99.9
6	60 minutes	20	0.2480	95.3

The data of Table 2 show that the oxidation of hypophosphorous acid by a solution of $NaICl_4$ without the addition of hydrochloric acid proceeds considerably more slowly than in a reaction mixture to which hydrochloric acid was added. The addition of small quantities of hydrochloric acid speeded the oxidation process, while great quantities of HCl led to reduction of the rate of oxidation of hypophosphorous acid.

So great a difference in the rate of oxidation of NaH_2PO_2 [~42 hours (experiment 3) and ~60 minutes (experiment 5)] under the above described conditions can be explained by the fact that in both cases the hypophosphorous acid being formed (but not its salt) is subjected to the action of hydrochloric acid, added (experiment 5) or appearing (experiment 3) as a result of the reduction of ICl_3 or ICl_4^- (equation 3).

This fact can further serve as one confirmation of the fact that only the active coordination-unsaturated tautomeric form of hypophosphorous acid undergoes oxidation; this form is absent, as was shown by A. I. Brodsky and L. V. Sulima [8], in the anion of its sodium salt.

We assumed that the oxidation process of hypophosphorous acid by iodine chloride could be speeded by heating and also by dilution with water (the latter lowers the concentration of the hydrochloric acid contained in the titrated solution of iodine chloride and, therefore, increases the quantity of I^+ ions in the solution).

However, dilution of the reaction mixture with water and increasing the temperature requires somewhat modifying the method of determination, as a consequence of the fact that the complex acid $H[ICl_2]$, contained in the hydrochloric acid solution of iodine chloride, dissociates according to the equation:

$$HICl_2 \rightleftarrows H^+ + ICl_2^-$$

$$ICl_2^- \rightleftarrows ICl + Cl^- .$$

Dilution with water, and also heating of the hydrochloric acid solutions of iodine chloride shifts the equilibrium to the right, in the direction of formation of a small quantity of free ICl molecules which undergo further hydrolysis with evolution of free iodine:

$$5ICl + 3H_2O \rightleftarrows 2I_2 + HIO_3 + 5HCl.$$

Thus, in such solutions it was impossible to conduct determination of hypophosphorous acid by the quantity of iodine evolved, since the chloroform also extracts the iodine formed as a result of the hydrolysis of iodine chloride. In such cases the determination has to end with decomposition of excess iodine chloride by potassium iodide with subsequent titration of the iodine with $Na_2S_2O_3$ solution.

To choose the optimal conditions for quantitative oxidation of sodium hypophosphite by ICl solution, experiments were set up in which the influence of excess iodine chloride, the time of reaction and the concentration of acid and dilution with water were studied. The results of these experiments are set forth in Table 3. For all experiments an approximately 0.1 N solution of $NaH_2PO_2 \cdot H_2O$ (0.2900 g/ 100 ml) was prepared. 5 ml of this solution was taken for each determination.

TABLE 3

The influence of various conditions on the oxidation of $NaH_2PO_2 \cdot H_2O$ by a hydrochloric acid solution of ICl

Amount added of 0.1 N ICl solution (in ml)	Amount of 0.1 N ICl solution taken up (in ml)	Quantity of water (in ml)	Temperature of the reaction mixture (in °C)	Duration of reaction (in minutes)	Amount of 1 N HCl solution added (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
						(in g)	(in %)
			Influence of excess ICl				
10	4.90	100	40-50	60	—	0.2597	89.50
15	5.43	100	40-50	60	—	0.2878	99.23
20	5.48	100	40-50	60	—	0.2904	100.15
25	5.53	100	40-50	60	—	0.2931	101.03
			Influence of the duration of the reaction				
25	2.10	100	40-50	5	—	0.1113	38.38
25	4.14	100	40-50	10	—	0.2194	75.65
25	5.31	100	40-50	30	—	0.2814	97.03
25	5.37	100	40-50	40	—	0.2846	98.10
			Influence of the acid concentration				
25	5.53	100	40-50	60	1	0.2931	101.03
25	5.36	100	40-50	60	5	0.2840	97.93
25	5.06	100	40-50	60	10	0.2680	92.41
			Influence of dilution with water and of the temperature of the reaction mixture				
25	3.90	—	20	60	—	0.2067	71.20
25	4.90	100	20	60	—	0.2597	89.50
25	5.50	50	40-50	60	—	0.2915	100.54
25	5.53	200	40-50	60	—	0.2931	101.03

As is evident from the data of Table 3, the oxidation of NaH_2PO_2 deteriorates without dilution with water. To obtain quantitative results it is necessary to add water heated to 40-50°; for complete oxidation, no less than 60 minutes are required; no less than a threefold excess of iodine chloride is necessary.

On the basis of these data we worked out the following method for quantitative determination: 0.25-0.3 g of hypophosphorous acid or of its sodium salt are dissolved in water in a 100 ml measuring flask. To 5 ml of the solution 100 ml of water heated to 40-50° is added and subsequently 15-20 ml of an 0.1 N solution of ICl and the solution is left for 1 hour. 10 ml of a 10% solution of potassium iodide is then added and the iodine which separates is titrated with 0.1 N sodium thiosulfate solution.

TABLE 4

Quantitative determination of $NaH_2PO_2 \cdot H_2O$ with a hydrochloric acid solution of ICl (5 ml of the starting solution taken)

Amount of the weighed portion of $NaH_2PO_2 \cdot H_2O$ (in g per 100 ml of the solution)	Amount of 0.1 N ICl solution taken up (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
		(in g)	(in %)
0.3170	6.00	0.3180	100.31
0.2810	5.30	0.2809	99.96

The results of the determinations are set forth in Table 4.

We also studied the reaction of sodium hypophosphite with a hydrochloric acid solution of iodine trichloride. As the experiment showed, iodine trichloride oxidizes hypophosphorous acid quanitatively into phosphoric acid. The reaction proceeds according to the equation:

$$3H_3PO_2 + 4ICl_3 + 6H_2O = 3H_3PO_4 + 2I_2 + 12HCl \quad (3)$$

or

$$3H_3PO_2 + 4ICl_4 + 6H_2O = 3H_3PO_4 + 2I_2 + 12HCl + 4Cl^- . \quad (3a)$$

However, we did not succeed in determining the quantity of iodine evolved, since the iodine reacts with excess iodine trichloride and is converted into iodine chloride according to the equation: $ICl_3 + I_2 = 3ICl$. Therefore, we had to determine the quantity of sodium hypophosphite (or H_3PO_2) oxidized by the amount of iodine trichloride consumed in the oxidation.

To choose the conditions for the quantitative oxidation of sodium hypophosphite or of H_3PO_2 with iodine trichloride solution, exactly the same experiments were set up for the study of the influences of the series of factors on the oxidation process as in the study of the action of iodine chloride.

The experiments showed that a reaction time of 60 minutes and a tenfold dilution with water heated to 60-70° was necessary for this. No less than a four- or fivefold excess of iodine trichloride was necessary.

TABLE 5

Quantitative determination of $NaH_2PO_2 \cdot H_2O$ with a hydrochloric acid solution of ICl_3 (5 ml of solution taken)

Amount of the weighed portion of $NaH_2PO_2 \cdot H_2O$ (in g per 100 ml of the solution)	Amount of 0.1 N ICl_3 solution used up (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
		(in g)	(in %)
0.2590	4.90	0.2597	100.27
0.2850	5.35	0.2835	99.49

The Method of Determination: 50-100 ml of water heated to 60-70° and 20-25 ml of 0.1 N iodine trichloride were added to 5 ml of approximately 0.1 N sodium hypophosphite solution and the solution was left for one hour. 10 ml of 10% potassium iodide solution was further added and the iodine evolved was titrated with 0.1 N sodium thiosulfate solution. It is evident from equation (3) that during the oxidation of 3 molecules of hypophosphorous acid, 4 molecules of iodine trichloride amounting to 16 equivalents of oxidizing agent, are used up. In the reaction 4 atoms of iodine are evolved, which, during the determination of excess iodine trichloride, are also titrated with sodium thiosulfate. Thus, in the oxidation of 1 molecule of hypophosphorous acid, (16 − 4) : 3 = 4 equivalents of oxidizing agent are actually used up.

The results of the determinations are set forth in Table 5.

SUMMARY

1. The reciprocal reactions of NaH_2PO_2 and H_3PO_2 with hydrochloric acid solutions of ICl and ICl_3 and with an aqueous solution of $NaICl_4$ reactions were studied.

2. The results of the investigations confirm the existence of two tautomeric forms of hypophosphorous acid, an inactive coordination-saturated, and an active coordination-unsaturated form with a free electron pair on the phosphorus.

The opinion of Orlov that the oxidation reaction of hypophosphorous acid with iodine proceeds by way of the addition to it of iodine was confirmed.

3. A method was worked out for the quantitative oxidation of NaH_2PO_2 and H_3PO_2 to phosphoric acid by iodine chloride and trichloride.

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CATALYSTS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE

G. M. Zhabrova, S. Z. Roginsky and E. A. Fokina

Heterogeneous catalytic processes proceeding in solutions vary among themselves in a number of particulars which are not involved in gaseous contact reactions, and these processes have been studied much less than the latter. Meanwhile, these processes are very widely used, and their investigation can elucidate new aspects of the mechanism of heterogeneous catalysis, of the laws governing the choice of catalyst and of the kinetics of catalytic reactions in solutions.

Influenced by these considerations, we undertook the investigation of the catalytic action of a number of solid oxides and salts on the decomposition of aqueous solutions of hydrogen peroxide.

Hydrogen peroxide is one of the most important active compounds which appeas in oxidizing reactions in solutions. Its decomposition can serve as a model reaction for more complex oxidation-reduction processes and, in addition, has great significance for biochemistry.

In our chemical literature a very considerable number of works has been devoted to the study of the catalytic decomposition of hydrogen peroxide. Arbuzov in 1914 [1] noted that the catalytic decomposition of hydrogen peroxide consisted of a reaction "the study of which, even a hundred years ago, was almost one of the most important sources for our understanding of the laws which are followed in catalytic processes."

In the investigations of Bakh [2] the decisive role of peroxides as active intermediate products in various oxidizing reactions in chemistry and biology was shown. Bakh [3] noted the probable existence of higher peroxides of hydrogen such as H_2O_4 and others.

In the middle of the 19th century, Khodnev [4] formulated the hypothesis that the decomposition of hydrogen peroxide in the presence of catalysts proceeds by way of the formation of intermediate compounds. Mendeleev [5] considered that during the decomposition of hydrogen peroxide on silver, water and silver oxide are formed; the latter during reaction with hydrogen peroxide evolves oxygen, being itself reduced to silver; this cycle is repeated many times. Silver oxide appears in the given case as an intermediate product formed during the reaction of catalyst with catalyzed substance.

The theory of intermediate compounds received further development in the works of Shpitalsky and his co-workers [6, 7] with reference to homogeneous catalysis of the decomposition of hydrogen peroxide. The works of Petin and his co-workers [8] and also the works of Bogdanov [9-11] are worth mentioning. Kobozev, Nikolaev and their co-workers [12-16] paid considerable attention to the decomposition process of hydrogen peroxide; particularly notable are their data concerning the catalytic decomposition of hydrogen peroxide under the influence of elementary ions, adsorbed on carriers and of ammoniates of various metals.

Teletov [17] carried out detailed catalytic decompositions of hydrogen peroxide on platinum.

Pisarzhevsky and his co-workers [18-21] investigated the decomposition of hydrogen peroxide in the presence of metallic and oxide catalysts and came to the conclusion that the passage of electrons from the catalyst to the reacting molecules of hydrogen peroxide plays an essential role in the mechanism of this process and that in a number of cases it is not the solid substance itself, but its ions in solution that are responsible for the catalysis.

A chain mechanism for the decomposition of solutions of hydrogen peroxide in the presence of ions of the heavy metals was established by Haber and Wilstätter and Weiss [22-24], who gave a detailed step-by-step reaction scheme. In the recently published investigations of Emanuel and Kruglikova [25] the authors came to the conclusion that homogeneous decomposition of hydrogen peroxide ought to be considered a chain reaction with side reactions. In the opinion of certain investigators, including Kazarnovsky and Neiding [26], in the decomposition of hydrogen peroxide there takes place a chain radical reaction; in the presence of alkali this leads to the increase in the reaction rate due to the strengthening of the electrolytic dissociation of the peroxide molecule.

In contrast to homogeneous decomposition for which the basic particulars of the mechanism have been established, although details remain unclear, the mechanism of the heterogeneous decomposition of hydrogen peroxide has been less studied and the enormous experimental material which has accumulated concerning this reaction has been insufficiently interpreted from a theoretical point of view. In this state of affairs, it is of considerable interest to trace the dependence of the catalytic activity of catalysts of the decomposition of hydrogen peroxide on the position of the elements entering into the composition of the catalysts in the Mendeleev periodic system, and on the electron and acid-base properties of the catalysts.

To conduct such a group of investigations involved methodological difficulties typical of catalysis in solution, involving such a chemically active reagent as hydrogen peroxide. Complications were produced by the appreciable solubility in hydrogen peroxide solution of a number of the catalysts investigated by us, the possibility of chemical reaction of hydrogen peroxide with the catalysts introduced by us and difusion difficulties.

Investigation of the rate of decomposition was conducted gasometrically.

The reaction apparatus was made of molybednum glass having the form of a "duck", placed in a hollow metallic cover, joined to a liquid thermostat and kept to a fixed temperature with a precision of ± 1°. The apparatus was joined to a gas burette with a fine rubber tube and was supported together with the cover on a stage of a shaking apparatus which permitted the intensity of agitation of the reaction mixture to be varied from 50 to 500 rocking oscillations per minute. As Elovich and Zhabrova [27] had shown earlier in an investigation of the catalytic hydrogenation of oil, such shaking is considerably more effective than the usual agitation for finely divided contact in liquid medium.

The order of conducting the experiments was as follows. Into the reaction apparatus, preliminarily heated to the given temperature, 20 ml of hydrogen peroxide solution was poured. After constant temperature was reached (usually after 20-30 minutes) a determined weighed portion of the catalyst equal to 0.1 g was placed in the solution. The apparatus was then closed with a stopper, the shaking apparatus was turned on and the time of beginning the reaction was noted to the second.

Comparison of the various contact reactions was conducted at 45°. It was established by preliminary experiments that both the rate of decomposition of hydrogen peroxide on the walls of the reaction vessel and the rate of homogeneous decomposition were much less than the rate of catalytic decomposition.

In working up the experiments a correction was introduced for the rate of the process of decomposition of hydrogen peroxide under analogous conditions but in the absence of catalyst. The reaction apparatus was prepared from the same sort of glass in all cases. The solution of hydrogen peroxide used in our investigations was prepared by dilution with twice distilled water of a 30% solution of perhydrol containing according to label 0.0005% chlorine, $SO_4^{=}$ 0.006%, $PO_4^{=}$ 0.005%, free acid (H_2SO_4) 0.003% and insoluble residue 0.04%.

It is noteworthy that many authors, in particular Shpitalsky and Konovalova [28], Dain and Epshtein [29], demonstrated that the catalytic decomposition of hydrogen peroxide proceeds at varying rates for preparations of various origins, due to the different quantities of catalytic agents (powder, positive homogeneous catalysts, contact poisons, and so forth) they contain. Taking these observations into account, we conducted all investigations with hydrogen peroxide of the same brand and lot. The concentration of the aqueous solution of hydrogen peroxide was verified by titration with 0.1 N potassium permanganate solution.

Before arranging the systematic comparison of the activities of the catalysts under study, it was necessary to satisfy ourselves that under the chosen conditions the process would not become kinetic. For this the influence of the intensity of the shaking on the rate of decomposition of hydrogen peroxide was investigated. As is evident from Fig. 1, the rate of the reaction on magnesium oxide does not depend on the intensity of the agitation. Analogous results were obtained for other catalysts, which indicates the absence of diffusion complications.

Special experiments were set up to observe the solutions of catalysts in aqueous solution of hydrogen peroxide and to elucidate the role of homogeneous catalysis. The catalysts in the quantities employed during the measurement of the reaction rate (0.1 g) were steeped in 20 ml of 2% hydrogen peroxide solution at a temperature of 45° for 5 hours, which exceeded the duration of the majority of the kinetic experiments. Further, the solution was filtered off from the catalyst, and 5 ml of the filtrate was added to 15 ml of a 2% solution of peroxide and measurements of the rate of the decomposition of hydrogen peroxide were conducted.* The results of these experiments are set forth in Figure 2. As is evident from the figure, the filtrates of the majority of the oxides possess a noticeable catalytic action, however their catalytic activity is significantly less than the activity of solid catalysts. The filtrate of a solution of hydrogen peroxide steeped with chromic oxide had considerable catalytic activity.

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* In addition to this, for the inactive catalysts the filtrate practically consisted of a solution of undecomposed hydrogen peroxide and for the active — of water. Thus, in the latter case we had to do with a somewhat more dilute solution of hydrogen peroxide during the course of the experiment, which, however, could not substantially affect the catalytic activity of the solutions under investigation.

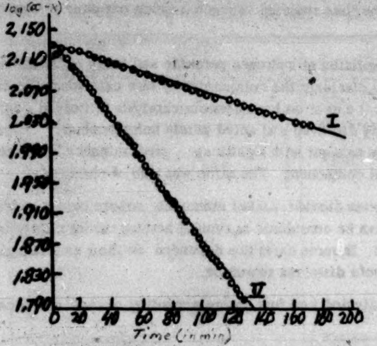

Figure 1. Non-dependence of the rate of decomposition reaction of hydrogen peroxide on the intensity of agitation of the reaction mixture (the intensity was changed in the course of the experiment from 120 to 440 rocking oscillations per minute). I − MgO; II − MgO, with antimony oxide as a promoter. a − initial quantity of H_2O_2; x − Quantity of reacted H_2O_2.

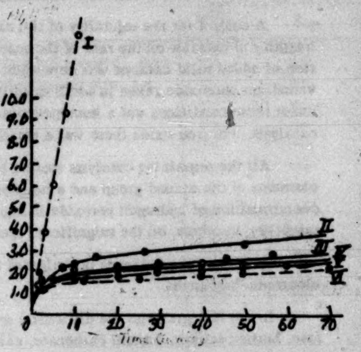

Figure 2. Decomposition of hydrogen peroxide in the presence of filtrates obtained after treatment of various oxides with a solution of hydrogen peroxide. I − Cr_2O_3 II − Fe_2O_3 III − BaO; IV − NiO; V − MgO; VI − thermal decomposition.

A second method of calculating the possible influence of homogeneous catalysis was the comparison of the actions of markedly different quantities of catalyst. The rate of heterogeneous process proceeding in the kinetic region, is directly proportional to the quantity of catalyst taken. It is difficult to expect strict adherence to this relationship during the simultaneous appreciable homogeneous catalysis of the dissolved portion of the catalyst.

Thus, from the data concerning the influence of quantity of the catalyst on the rate of the process one can obtain additional (kinetic) indications concerning the possible role of homogeneous catalysis in the decomposition of hydrogen peroxide. Such verification was conducted with a number of catalysts. The quantity of catalyst taken for the investigation was varied tenfold while keeping all other conditions constant (concentration of hydrogen peroxide, its temperature and the rate of agitation). In Fig. 3 are set forth examples of the influence of the quantity of catalyst during strong homogeneous catalysis (Cr_2O_3). In Fig. 4, the basic process is also heterogeneous (MgO). As is evident from Fig. 3, the rate of decomposition of hydrogen peroxide in the presence of chromic oxide increases considerably more slowly than the increase in quantity of catalyst and the decomposition proceeds, self-accelerated. This indicates the complexity of the process, since here, evidently, simultaneous solution of the catalyst (which was noted by the appearance of coloration) takes place, and chemical change of the form of the catalyst occurs.

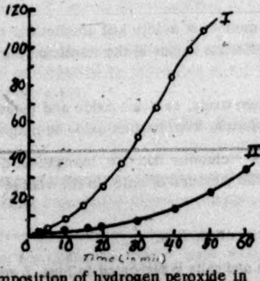

Fig. 3. Decomposition of hydrogen peroxide in presence of various quantities of chromic oxide at 45°. I − 0.1 g Cr_2O_3; II − 0.01 g Cr_2O_3

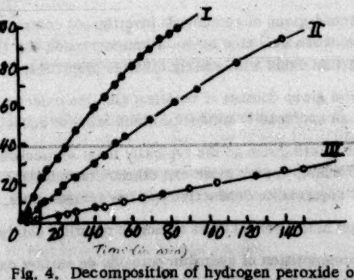

Fig. 4. Decomposition of hydrogen peroxide on magnesium oxide (quantity of magnesium oxide varied by factors of 5 and 10). I − 1.0 g MgO; II − 0.5 g MgO; III − 0.1 g MgO.

As is evident from Fig. 4, the character of the kinetic curves for the catalysis on magnesium oxide is not changed with increase in the quantity of catalyst, but the time required to reach a given per cent of conversion falls reciprically to the increase in the quantity of catalyst.

A control for the solubility of the catalyst in the solution of hydrogen peroxide and study of the influence of the quantity of catalyst on the rate of the reaction served to elucidate the comparatively rare case when the catalytic action of added solid catalyst was dependent to a significant extent on homogeneous catalysis (dissolved contact). Thus, vanadium pentoxide taken in small quantities completely dissolved and acted purely homogeneously. Chromic oxide under these conditions was a homogeneous-heterogeneous catalyst with significant predominance of homogeneous catalysis. For iron oxide there was a small homogeneous component. The same was true of chromites.

All the remaining catalysts studied by us — manganese dioxide, nickel monoxide, copper oxide, oxides of the elements of the second group and a number of others — can be considered as typical heterogeneous catalysts of the decomposition of hydrogen peroxide in aqueous solutions. In some cases this depended on their exceedingly small solubility, in others, on the insignificant specific activity of a dissolved substance.

All the solid substances investigated by us can be divided into four groups according to their chemical and electronic properties.

In the first group go the difficultly soluble colorless salts which do not contain transition elements — lead sulfate, barium sulfate, barium carbonate, calcium carbonate, aluminum silicate.

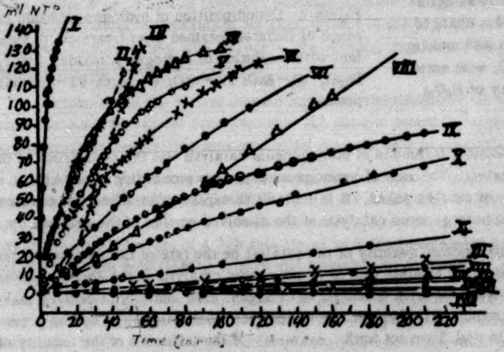

Fig. 5. Decomposition of hydrogen peroxide on various catalysts. I — MnO_2; II — V_2O_5; III — Cr_2O_3; IV — CuO; V — Fe_2O_3; VI — NiO; VII — CaO; VIII — BaO_2, IX — BaO; X — Y_2O_3; XI — MgO; XII — La_2O_3; XIII — ZnO; XIV — CdO; XV — TiO_2; XVI — aluminum silicate; XVII — Al_2O_3; XVIII — SnO_2.

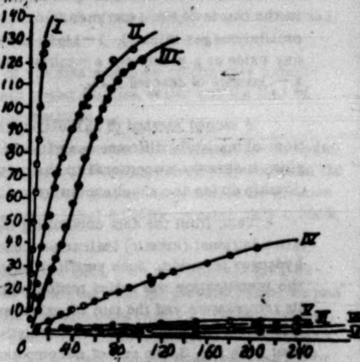

Fig. 6. Decomposition of hydrogen peroxide on the carbonates of transition and non-transition elements. I — $NiCO_3$; II — $Fe_2(CO_3)_3$; III — $MnCO_3$; IV — $MgCO_3$; V — $CdCO_3$; VI — $BaCO_3$; VII — $ZnCO_3$; VIII — $CaCO_3$.

The second group of compounds investigated contained a number of acidic and amphoteric colorless oxides — stannic oxide, silica gel, zinc oxide, aluminum oxide and the colorless oxides of the transition elements — lanthanum oxide and yttrium oxide with weakly alkaline properties.

The third group consists of colorless alkaline oxides — barium oxide, calcium oxide and magnesium oxide. All these possess an appreciable solubility which falls for aqueous solutions from barium oxide to magnesium oxide.

Into the fourth group go the typically ionic semiconductors — chromic trioxide, manganese dioxide, nickel monoxide, ferric oxide, copper oxide and others, characterized by the presence of color in the visible portion of the spectrum and appreciable conductivity at low temperatures.

Platinum black was taken as an active metallic catalyst for comparison.

The decomposition of hydrogen peroxide on various oxides and salts is presented in Figs. 5 and 6.

The data characterizing the comparative activity of various kinds of oxides and salts are presented in the table.

TABLE

Comparative activity of various oxides and salts at 45°

No.	Designation of the catalyst	Color	$K = \frac{1}{\tau_{50\%}}$ (min. $^{-1}$)	$S \frac{M^2}{g}$	$K_{sp.}$
1	$PbSO_4$	White	Reaction practically does not proceed. Rate of decomposition extraordinarily slow, i.e., $\frac{1}{\tau_{50\%}} < 0.001$	—	—
2	$BaSO_4$			—	—
3	$CdSO_4$			—	—
4	$ZnCO_3$			—	—
5	$CaCO_3$			—	—
6	$BaCO_3$			—	—
7	$MgCO_3$			—	—
8	$MnCO_3$	Rose	0.00280	—	—
9	$Fe_2(CO_3)_3$	Light brown	0.02218	—	—
10	$NiCO_3$	Green	0.0415	—	—
			0.125		
11	Silica gel	White	Rate of decomposition of hydrogen peroxide extraordinarily small, i.e., $\frac{1}{\tau_{50\%}} < 0.001$	300	—
12	Aluminum silicate	Cream		165	—
13	Al_2O_3	White		—	—
14	SnO_2			—	—
15	TiO_2			14.8	—
16	CdO	Brown	The same	6.0	—
17	La_2O_3*	White	0.0010	—	—
18	ZnO*		0.0010	20.0	0.000050
19	MgO*		0.0017	32.0	0.000053
20	Y_2O_3		0.0047	—	—
21	BaO		0.0076	17.5	0.00044
22	BaO_2		0.0097	—	—
23	CaO		0.0150	18.0	0.00083
24	NiO	Greyish black	0.0232	11.6	0.0093
25	Fe_2O_3	Brown	0.0294	10.2	0.002
26	Cr_2O_3**	Black	0.0286	—	—
27	CuO		0.031	—	—
28	MnO_2		0.5	6.7	0.075
29	V_2O_5***	Brown	0.045	15.0	0.003
30	$MgCr_2O_4$	Green	0.0150	49	0.0004
31	$CuCr_2O_4$	Black	0.0164	1.5	0.011
32	$CuAl_2O_4$	Light brown	0.0133	6.7	0.002
33	$FeCr_2O_4$	Red-brownish	0.00125	1.6	0.00078
34	Pt (black)	Black	Reaction completed in 1 minute		

The conventional index of activity in the decomposition of hydrogen peroxide is expressed as the reciprocal magnitude of the half time of decomposition $K = \frac{1}{\tau_{50\%}}$ (min. $^{-1}$).

Parallelly with the measurement of the catalytic activity, for a number of catalysts the magnitudes of their specific surface as measured by adsorbtion of the vapors of n-heptane were determined. These quantities are set forth in column 5 of the table.

As is evident from the table and Fig. 5, the catalyst-oxides containing transition elements and possessing an intense color, are more active than the colorless catalysts and those catalysts consisting of non-transition elements.

The difference in activity of these catalysts is very great. Thus, manganese dioxide, distinguished by its dark color and including a transition element (manganese), has a specific activity 1400 times greater than the colorless oxide of magnesium, which does not contain a transition element and 171 times greater than barium oxide. Platinum black is distinguished by an exceptionally great activity. The rules applying to the oxides are accurate for the carbonates of the transition and non-transition elements.

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* In these cases the quantities $\frac{1}{\tau_{50\%}}$ were obtained by extrapolating the kinetic curves.

** The solution had a reddish color.

*** The catalyst was practically completely dissolved at the time of the experiment

As is evident from Fig. 6, the carbonates of nickel, iron and manganese possess the greatest catalytic activity; these contain transition elements and have an intense coloration; the colorless carbonates of magnesium, cadmium, barium and zinc oxide characterized by a significantly less activity.

Of the 14 colored catalysts investigated by us, 13 comply with the given relationship, and only one — iron chromite (Fig. 7) — is distinguished by a small activity. It is probably not by chance that the colored cadmium oxide, not containing a transition element, is little active. In comparing the activity of the catalysts investigated, it should be noted that the general rule for selection of catalysts, ensuing from the classification of the catalysts and of the catalytic processes assumed by one of us [30, 31] for reactions of the oxidation-reduction type, is demonstrably correct for the decomposition of hydrogen peroxide. The catalytic activity of the catalysts for this reaction depends on the position in the Mendeleev periodic system of the elements entering into the composition of the catalysts, and on the intensity of the coloration.

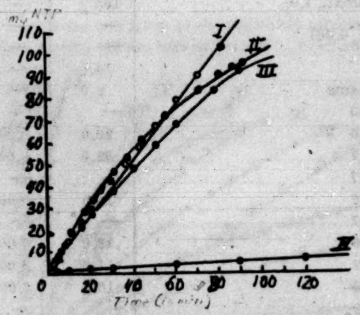

Fig. 7. Decomposition of hydrogen peroxide on chromites and aluminates. I — $CuCr_2O_4$; II — $MgCr_2O_4$; III — $CaAl_2O_4$; IV — $FeCr_2O_4$.

It should be noted that in contrast to the previously investigated process of deep oxidation of hydrocarbons [32], where the above indicated laws completely determined the activity of the contacts, in the given case a second law for the selection of catalyst is manifested that was not previously observed for the oxidation-reduction reactions; as is evident from the data set forth in the investigation of colorless oxides of the alkaline earths and rare elements, their catalytic activity increases with increase of their alkaline properties. Thus, of the oxides of the alkaline earth elements, magnesium oxide is less active than the oxides of calcium and barium. The oxides of the rare earth elements such as lanthanum, are more weakly alkaline and have less catalytic activity. Yttrium oxide is an exception. At the same time, compounds possessing acidic and amphoteric properties are distinguished by an exceedingly small catlytic activity: stannic oxide, aluminum oxide, titanium dioxide, zinc oxide, aluminum silicate. It should be noted that in all cases the method of preparing the catalysts influences the catalytic activity. In our investigations, therefore, in which in part ready made preparations were employed and in part preparations prepared by various methods, there was naturally a small deviation from the regular distribution of oxides and salts according to their catalytic activity deduced from their position in the periodic system of elements. Thus, our preparation of barium oxide was somewhat less active than calcium oxide, yttrium oxide was more active than magnesium oxide and so forth.

On the basis of our data one can speak only of general qualitative regularities.

The question concerning the detailed mechanism of the action of contact reactions involving the decomposition of hydrogen peroxide will be analyzed separately. We note here that the connection of catalytic activity with the electronic properties of the elements entering into the composition of the catalysts indicates a role for the direct exchange of electrons in the given process, while the influence of alkalinity may be associated with the increase in content of HO_2^- and O_2^- ions, which are decomposed more readily than the H_2O_2 molecule.

SUMMARY

1. The catalytic activity of a number of oxides and salts with reference to the decomposition of hydrogen peroxide in aqueous solutions was investigated.

2. In certain cases (V_2O_5, Cr_2O_3, and also partially Fe_2O_3) the homogeneous catalytic action of dissolved catalyst has an essential significance in the decomposition of hydrogen peroxide. This action is probable as a weaker secondary effect in several other cases (chromites, ferrites, oxides of the alkaline earth metals).

3. The activity of the catalysts depends on the position of the elements of which they are composed in the Mendeleev periodic system and on the chemical properties of the solid compounds. Catalysts containing transition

elements and possessing an intensive coloration as a rule are considerably more active than colorless catalysts not containing transition elements and than colored compounds not containing transition elements.

4. The catalytic activity of colorless alkaline oxides is significantly higher than the activity of colorless acid oxides and in general increases with increasing alkalinity.

5. A hypothesis concerning the various mechanisms by which the free electrons of the solids and the alkalinity of their surfaces influence the decomposition of hydrogen peroxide was proposed.

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REACTION OF DIFFICULTLY SOLUBLE SALTS WITH CATIONIC SUBSTANCES

A. G. Koblyansky

The properties of ion exchange resins and their practical uses are the subjects of thorough study at the present time [1]. However, certain peculiarities in the behavior of these substances are still insufficiently elucidated. In particular, the question of the behavior of precipitates of various difficultly-soluble salts in the presence of ion exchange resins appears not to have been studied. The present work has as its goal to at least partially fill this gap.

If in a two phase system consisting of a difficultly-soluble salt, for example $BaSO_4$ and its saturated solution, one introduces a cationic substance in say, its sodium form RNa, then as a result of ion exchange the cationic salt will be bound by the ion exchange resin and sodium ions will pass over into the solution.

$$BaSO_4\,(solid) \rightleftharpoons Ba^{2+} + SO_4^{2-}\,, \qquad (1)$$

$$2RNa + Ba^{2+} \rightleftharpoons R_2Ba + 2Na^{+}\,. \qquad (2)$$

The equilibrium described by equation (1), is upset and a new portion of barium sulfate will pass over into solution. The salt will continue to dissolve as long as equilibrium in our system is not established between an aqueous solution and both solid phases — the salt and the cationic substance. In conformity with this in the moment of equilibrium there should be observed two conditions:

1) The number of barium ions absorbed by the cationic substance from the solution in unit time should be equal to the number of barium ions dislodged from the cationic substance in the same interval of time;

2) The equilibrium concentrations of barium ions and sulfate ions should satisfy the solubility product of barium sulfate.

Thus, the solubility of difficultly-soluble precipitates of a salt during their reaction with cationic substances should be determined, on the one hand by the solubility product of the salt, and on the other hand by the exchange capacity of the cationic substance, which in its turn depends on the properties of the ion exchange resin and on the properties of the adsorbed ion — on its capacity for exchange.

The behavior of the oxalates, sulfates and carbonates of the alkaline earth metals in the presence of cationic substances was studied in the present work. The bulk of the experiments were conducted with the cationic substance SBS in its sodium and hydrogen forms. Certain important conclusions were verified for sulfocarbon and P-vofatite.

The method of conducting the determinations was as follows. A weighed portion of the salt, a weighed portion of the cationic substance and a determined volume of water were introduced into a flask with a ground glass stopper. After the flask had been shaken for three hours at room temperature (20-22°), the contents of the flask were filtered through a dry filter. During the reaction of the cationic substance with the difficultly soluble salts either the corresponding free acids or their sodium salts were added dropwise to the solution:

$$SrC_2O_4 + 2RH \rightleftharpoons H_2C_2O_4 + R_2Sr,$$

$$CaCO_3 + 2RNa \rightleftharpoons Na_2CO_3 + R_2Ca.$$

The solution of sodium carbonate was titrated with 0.05 N hydrochloric acid in the presence of methyl red. The content of sodium oxalate was determined by titration with 0.025 N potassium permanganate. The sodium sulfate was converted into sulfuric acid, the solution was passed through a column containing H-cationite (the hydrogen form of the cationic substance) and titrated with 0.04 N sodium hydroxide in the presence of methyl red. To determine the content of free acid formed in the systems with the hydrogen form of the cationic substance, sodium hydroxide was also employed.

The data obtained during the analysis of the aqueous solution permitted the equilibrium concentration of the ions in the system under investigation to be calculated. The results of the titration directly give the equilibrium concentration of the anions in aqueous solution. Only the oxalic acid solutions in which the concentration of oxalate ions can be considered constant [2], numerically equal to the second dissocation constant ($K_2 = 6.4 \cdot 10^{-5}$), are an exception.

Knowing the equilibrium concentration of the anions and the solubility product of the difficultly-soluble salt [3], one can find the equilibrium concentration of the cations of this salt in aqueous solution. The values of the solubility products were reduced, where this was possible, to 20°.

The total quantity of salt or acid contained in aqueous solution was equivalent to the total quantity of the cations of the difficultly soluble salt adsorbed by the cationic substance. Using this relationship, one can readily calculate the equilibrium concentration of the cations of the difficultly soluble salt in the cationic substance or, in other words, the magnitude of the absorbtion by the cationite in saturated solution of the difficultly-soluble salt under static conditions:

$$\text{Magnitude of absorption} = \frac{\text{normality of the solution} \cdot \text{volume of the solution (in milliliters}}{\text{amount of the weighed portion of cationite (in grams)}} \quad \frac{\text{mg-equiv.}}{\text{g}}$$

The figures set forth in Tables 1 and 2 indicate that all the salts investigated exchange ions with the cationite and as a result partially go over into solution. This capacity of difficultly-soluble salts for ionic exchange can be given a quantitative value, showing either the equilibrium concentration of the cations of the salt under investigation in the cationite (the graph following Tables 1 and 2), or the equilibrium concentration of salt or acid in the aqueous solution. Each of these figures will uniquely characterize the solubility of the difficultly soluble salt in the presence of the given cationite only during some constant relationship of the quantities of the aqueous solution and the ion exchange resin. In our experiments the volume of water was always equal to 20 ml and the weighed portion of air-dry cationite SBS was equal to 0.4 g.

TABLE 1

Equilibrium in the system: difficultly soluble salt-water-sodium form of the cationite SBS

Amount of weighed portions of salt – 0.1 g, volume of water – 20 ml, amount of weighed portions of cationite – 0.4 g

Salt	Solubility product of salt	Equilibrium concentration		
		of anions in aqueous solution (g-ion/liter)	of cations of the salt in aqueous solution (g-ion/liter)	of cations of the salt in the cationite (mg-equiv/g)
Barium oxalate	$1.62 \cdot 10^{-7}$	$1.1 \cdot 10^{-2}$	$1.5 \cdot 10^{-5}$	1.1
Strontium oxalate	$5.6 \cdot 10^{-8}$	$9.1 \cdot 10^{-3}$	$6.2 \cdot 10^{-6}$	0.91
Calcium oxalate	$2.0 \cdot 10^{-9}$	$1.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-6}$	0.15
Strontium sulfate	$2.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-2}$	$2.5 \cdot 10^{-5}$	1.1
Barium sulfate	$9.3 \cdot 10^{-11}$	$4.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-7}$	0.048
Barium carbonate	$7.4 \cdot 10^{-9}$	$5.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-6}$	0.51
Strontium carbonate	$9.42 \cdot 10^{-10}$	$4.2 \cdot 10^{-3}$	$2.2 \cdot 10^{-7}$	0.42
Calcium carbonate	$7.4 \cdot 10^{-9}$	$5.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-6}$	0.50

TABLE 2

Equilibrium in the system: difficultly soluble salt-water-hydrogen form of cationite SBS

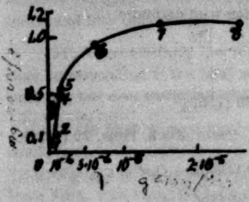
Volume of water – 20 ml, amount of weighed portion of cationite – 0.4 g

Salt	Amount of weighed portion of salt (g)	Equilibrium concentration			
		of acid in aqueous solution (g-equiv/liter)	of anions in aqueous solution (g-ion/liter)	of cations of the salt in aqueous solution (g-ion/liter)	of cations of the salt in the cationite (mg-equiv/g)
Barium oxalate	0.200	$3.1 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$2.5 \cdot 10^{-3}$	1.6
Strontium oxalate	0.200	$3.0 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$8.7 \cdot 10^{-4}$	1.5
Calcium oxalate	0.100	$2.0 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$	1.0
Strontium sulfate	0.100	$1.9 \cdot 10^{-2}$	$9.5 \cdot 10^{-3}$	$2.9 \cdot 10^{-5}$	0.95
Barium sulfate	0.100	$1.9 \cdot 10^{-4}$	$9.5 \cdot 10^{-5}$	$9.8 \cdot 10^{-7}$	0.0095

According to the literature data [4], the ions of the alkaline earth metals have very close exchange properties. Especially arranged experiments showed that the statistical exchange capacity [5] of the hydrogen form of cationite SBS in 0.1 N solutions of the chlorides of calcium, strontium and barium, determined by the method used in the present work, remained almost constant and equal to 1.5 mg/equiv/g. It may be concluded from this that in saturated solutions of difficultly-soluble salts the magnitude of absorption of the cationite depends little on the individual peculiarities of the ions of the various alkaline earth metals. Therefore, it can be considered that in all the systems studied, we had to do with perhaps one and the same cation and that the state of equilibrium must be determined by the concentrations of these cations. Actually, the figures set forth in Table 1 are evidence that the basic factor determining the solubility of a salt during the reaction with cationite is its solubility product. The less the solubility product of the salt, the more difficult the exchange between the ions and the cationite, and the less the magnitude of the absorption of the cationite in a saturated solution of this salt. This condition is true not only of salts of the same acid — for sulfates, oxalates, carbonates separately; it appears to be true also in relation to the entire aggregate of difficultly-soluble salts of calcium, strontium, and barium, regardless of which anion these salts contain. Salts with solubility products of the order of 10^{-7} react quite well with cationite. The equilibrium concentration of these salts for the sodium form of cationite SBS amounts to more than 1 mg-equiv/g. In salts with solubility products close to 10^{-10}, the ion exchange is insignificant.

Only strontium carbonate ($K_s = 9.4 \cdot 10^{-10}$) appears to be an exception to this rule: in the presence of the sodium form of the cationite (Table 1) this salt dissolves better than calcium oxalate ($K_s = 2 \cdot 10^{-9}$).

In systems containing the hydrogen form of cationite (Table 2), the oxalates of the alkaline earth metals display enhanced solubility in comparison with the sulfates: strontium oxalate ($K_s = 5.6 \cdot 10^{-8}$) passes over into solution more readily than strontium sulfate ($K_s = 2.8 \cdot 10^{-7}$). This phenomenon is caused by the fact that oxalic acid in comparison with sulfuric acid is a much weaker electrolyte. Therefore, in an equilibrium system: oxalate of an alkaline earth metal-water-hydrogen form of cationite, along with the two conditions for equilibrium, noted above, one additional condition must be observed: the equilibrium concentrations of the ions and the undissociated molecules of oxalic acid must satisfy its dissociation constants. The hydrogen ions displaced from the cationite as a result of ion exchange will give with the oxalate ions undissociated molecules, and thus will exert supplementary dissolving action on the oxalate residue.



Dependence of the magnitude of absorption of the sodium form of cationite SBS in saturated solutions of oxalates, sulfates and carbonates of the alkaline earth metals on the equilibrium concentrations of the cations of these metals in aqueous solution. 1) $BaSO_4$, 2) CaC_2O_4, 3) $SrCO_3$, 4) $CaCO_3$, 5) $BaCO_3$, 6) SrC_2O_4, 7) BaC_2O_4, 8) $SrCO_4$.

The functional dependence linking the equilibrium concentrations of the ions of the alkaline earth metals in aqueous solution and in the ion-exchange resin (Table 1), can be depicted graphically.

The smooth form of the curve shows that in calculating the equilibrium concentrations of the ions without taking account of their activity coefficients, we obtain comparable results which basically reflect correctly the regularities which are observed during the distribution of the cations between the aqueous solution and the ion exchange resin.

A sharp increase in the equilibrium concentrations of the cations of the alkaline earth metals in the ion exchange resin is observed only in the initial portion of the curve for exceedingly dilute solutions ($10^{-6} - 10^{-5}$ g-ion/liter). The cationite extracts approximately 1 g-equiv/g from a solution containing 10^{-5} g-ion/liter. During further increase in the concentrations of the water solution, the magnitude of the absorption for cationite SBS changes very slowly. As was noted above, the static exchange capacity of the hydrogen form of cationite SBS in 0.1 N solutions of the chlorides of calcium, strontium and barium amounts to 1.5 mg-equiv/g.

It is evident from Table 2 that the hydrogen form of cationite SBS absorbs the ions of the alkaline earth metals more poorly than its sodium form.

The data concerning the solubility of difficultly-soluble salts in

TABLE 3

Change in the acidity of an aqueous solution in the system: mixture of sulfates of barium and strontium-water-hydrogen form of cationite SBS as a function of the strontium sulfate content. Weighed portions of barium sulfate — 1 g, volume of water — 20 ml, weighed portion of cationite — 0.4 g

Amount of strontium sulfate introduced (in g)	Amount of 0.03817 N sodium hydroxide (in ml) consumed in the titration of 10 ml of the solution
0.05	4.57
0.02	2.30
0.01	1.11
–	0.20

the presence of ion exchange resins can be utilized for resolving certain practical problems. If the solubility product of a salt is very small, then a small admixture of another more soluble electrolyte should strongly affect the equilibrium concentrations of the ions in aqueous solution. Study of the behavior of mixtures of the sulfates of barium and strontium showed (Table 3) that even in the presence of 1% strontium sulfate, the acidity of the solution was sharply increased.

The use of the process of ion exchange as a rapid method for assaying the purity of difficultly soluble salts is suggested.

SUMMARY

1. It was established that in the reaction of difficultly-soluble salts with cationite in the presence of water the partial solution of these salts proceeds as a result of ion exchange.

2. The magnitude of the absorption for cationite SBS was determined in saturated solutions of the oxalates, sulfates, and carbonates of the alkaline earth metals under static conditions.

3. It was shown that the basic factor determining the solubility of difficultly-soluble salts in the reaction with cationite is the solubility product of these salts.

4. A curve was drawn for the magnitude of the absorption of cationite SBS in saturated solutions of the oxalates, sulfates and carbonates of the alkaline earth metals as a function of the equilibrium concentrations of the cations of these metals in aqueous solution.

5. A method was proposed for detecting insignificant admixtures of strontium sulfate in barium sulfate, based on the marked difference in the solubility of these salts during their reaction with cationite.

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* See Consultants Bureau Translation, page 153.

CHEMICAL REACTIONS IN VANADIUM PENTOXIDE – POTASSIUM SULFATE AND VANADIUM PENTOXIDE – POTASSIUM PYROSULFATE SYSTEMS

G. K. Boreskov, V. V. Illarionov, R. P. Ozerov and E. V. Kildisheva

Vanadium pentoxide, the basic component of vanadium catalysts for oxidizing sulfur dioxide, in the pure form possesses weak catalytic activity, which is rapidly increased by addition of salts of the alkaline metals [1]. Newmann [2] attempted to elucidate this sharply expressed promoter action by forming alkaline metavanadates.

It was, however, shown by further investigations [3] that the metavanadates of potassium and sodium are destroyed under the conditions of the catalytic oxidation of sulfur dioxide with the formation of the corresponding sulfates and pyrosulfates. It was also discovered that in the working vanadium catalysts, the bulk of the alkaline addition was found in the form of the sulfate or the pyrosulfate, regardless of what kind of compound was initially introduced into the catalyst.

At a comparatively low temperature and high partial pressure of sulfuric anhydride, that is, under conditions corresponding to the final stage of the oxidation of sulfur dioxide, pyrosulfate is formed; at higher temperatures and low concentrations of SO_3 in the gas, the sulfate of the alkaline metal is stable.

On the basis of what has been related we sought with interest, from the point of view of elucidating the mechanism of the promoter action of compounds of potassium on vanadium pentoxide, to study the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$, which are only unconditionally models to the extent that in vanadium catalysts, along with V_2O_5, they are present in the early stages of oxidation of vanadium, in quantities which depend on the temperature and the content of SO_2 in the gas.

EXPERIMENTAL

The system $V_2O_5-K_2SO_4$ was investigated, in a preliminary fashion, by one of us and M. A. Guminskaya. The data obtained, of a qualitative character, showed the presence of a eutectic with a melting point of about 450°.

Vanadium pentoxide, and potassium sulfate and pyrosulfate were the starting materials in our investigations. Commercial vanadium pentoxide was converted into ammonium vanadate by treatment with ammonia solution. The precipitate was dissolved in hot water and freed from mechanical admixtures. We proceeded further by the method of one of us and E. E. Ruderman [4]. The preparation obtained by this method was heated in a stream of oxygen at 400-450° for one hour. The latter operation was added by us in order to exclude the possible partial reduction of the pentoxide in the process of mechanical grinding [5]. Chemically pure potassium sulfate was twice recrystallized.

Potassium pyrosulfate was prepared according to the method of Cambi and Bozza [6] by heating potassium sulfate at 420-450° in a stream of dry air containing 5% SO_3. The gaseous mixture was obtained by preliminary conversion of the mixture of dry air with 5% SO_2 on a vanadium catalyst at 470°. The melting point of the potassium pyrosulfate was comparatively low, as a result of which the preparation was covered with a layer of melted pyrosulfate and the process of further sulfatization was retarded. Therefore, the salt treated by us was cooled in a stream of dry SO_3 to 350°, and then was finely divided in a stream of dry air and again treated with the indicated gaseous mixture at high temperature. This sequence of treatment was repeated until complete conversion of the sulfate into the pyrosulfate was achieved. The criterion of purity was the melting point. The preparation obtained agreed according to analysis, exactly with the composition $K_2S_2O_7$ with m.p. 407°, in contrast to that indicated by the Italian authors at 414.2° [6].

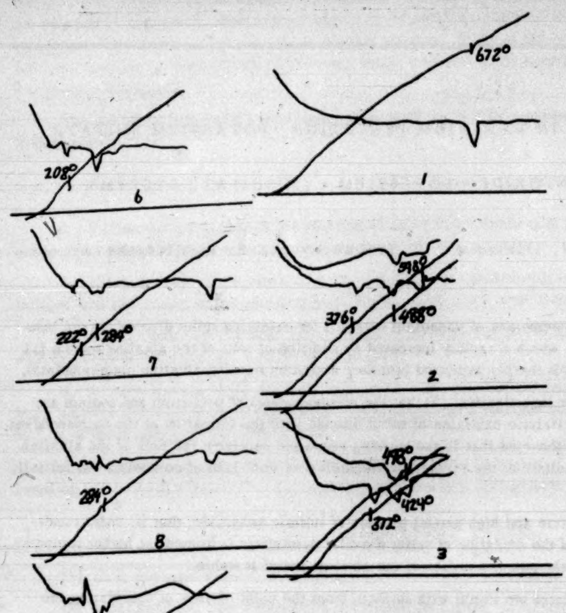

Fig. 1. Thermograms of fusion cakes of the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$. 1) Pure V_2O_5; 2) Batch of 0.2 mole-portion of K_2SO_4; 3) Batch of 0.5 mole-portion of K_2SO_4; 4) Batch of 0.8 mole-portion of K_2SO_4; 5) Pure K_2SO_4; 6) Pure $K_2S_2O_7$; 7) 0.2 mole-portion of $K_2S_2O_7$; 8) 0.3 mole-portion of $K_2S_2O_7$; 9) 0.5 mole-portion of $K_2S_2O_7$; 10) 0.7 mole-portion of $K_2S_2O_7$. In all thermograms, with the exception of the third, the upper transcription – the starting mixture, the lower transcription – repeated heating; in the third, the reverse is true.

All the initial compounds obtained were investigated roentgenographically. Roentgenological analysis showed that vanadium pentoxide possessed a rhombohedral lattice with parameters a = 11.48 Å, b = 4.36 Å, and c = = 3.55 Å, which was in agreement with the data published earlier [7, 8]. The roentgenograms obtained with powdered potassium sulfate and pyrosulfate were identical with the literature data [9].

Method of Investigation

Carefully ground preparations were mixed in the necessary proportions. The mixtures, in quantities of about 5 g, were stirred in a quartz Stepanov vessel (capacity 6-8 ml), in which the thermal investigations were conducted. The system $V_2O_5-K_2SO_4$ was investigated in open vessels but the system $V_2O_5-K_2S_2O_7$ in sealed vessels. Batches of the second system were placed in vessels which were then evacuated with a Gede pump to 10-15 mm residual pressure and sealed under a vacuum in order to avoid substantial change of the composition during heating, as a result of thermal decomposition and the volatilization of SO_3 associated with it (due to the high dissociation tension of pyrosulfate). The recordings of the cooling curves were conducted on a potentiometric installation with a chromal-alumel thermocouples. Compensation was accomplished on a sensitive slide wire cylinder and the current strength in the auxiliary circuit was held constant all the time with the aid of a manganin resistance box and controlled with a galvanometer. The rate of cooling was of the order of 2° per minute.

The heating curves were taken on a Kurnakov pyrometer with platinum-platino-rhodium thermocouples.

The fusion cakes obtained were ground in an agate mortar and subjected to roentgenostructural and chemical analyses.

The roentgenograms of all samples were taken with a copper emission spectrum in a truncated Debye chamber with a cell diameter of 92 mm. Inasmuch as the copper emission stimulates the secondary isotropic emission of vanadium, fogging the roentgenograms, with the exception of samples with a low V_2O_5 content, aluminum foil was placed around the film.

The content of SO_3, V_2O_5, and V_2O_4 was determined by chemical analysis of the fusion cake.

The System $V_2O_5-K_2SO_4$. The heating curves and the cooling curves were taken for the pure components and their mixtures in one tenth molar portions (Fig. 1).

The greatest interest attaches to the endothermic effect on the heating curve, observed in the entire composition interval and lying close to 380°. On the cooling curve this effect is absent, nor arising during repeated heating of the mixtures, which is evident from comparison of the thermograms on Fig. 1. If we take into account, aside from this, that this effect is not detected in the pure components taken separately, and is most strongly expressed in a mixture of $0.5V_2O_5-0.5K_2SO_4$, then it must be explained by reaction of vanadium pentoxide with potassium sulfate.

The remaining thermal effects observed, compared on the curves of cooling and heating and repeated heating, can be comparatively briefly discussed.

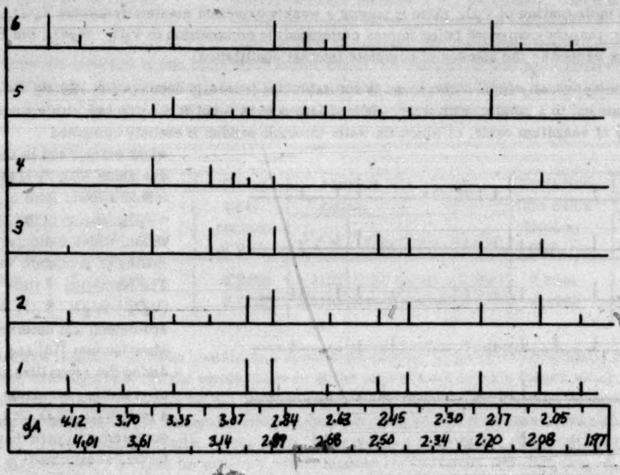

Fig. 2. Roentgenogram chart of the system $V_2O_5-K_2SO_4$. 1) Pure K_2SO_4, 2) 40% V_2O_5, 3) 50% V_2O_5, 4) 60% V_2O_5, 5) 70% V_2O_5, 6) pure V_2O_5.

It is very material that both connodes of the eutectic breaks in continuity lie on different temperature levels. This appears to be an unmistakable demonstration of the formation of compounds, although a dystectic maximum was not established by us.

All the fusion cakes were ground and subjected to roentgenologic structural investigation. While the roentgenograms of the pure components were legible, the fusion cakes gave a very strong fogging, evoked by the presence of an isotropic vitreous phase, and a number of somewhat weakened diffraction lines. The maximum intensity of these lines on the roentgenogram of a fusion cake containing 0.5 mole-portions of V_2O_5 could not be related to one of the starting components and belonged, consequently, to an unknown compound among them. On Fig. 2 is set forth a part of the scheme of roentgenograms.

TABLE 1

Composition of the fusion cake		Amount of weighed sample (in g)	Theoretical content of V_2O_5	Aqueous extract		Residue		Total content calculated as V_2O_5	Content of SO_3	
V_2O_5 (in moles)	K_2SO_4 (in moles)			V_2O_5	V_2O_4	V_2O_5	V_2O_4		Theoretical	In the aqueous extract
0.7	0.3	0.4995	0.3496	0.0091	None	0.3342	0.0033	0.3469	0.0688	0.0650
0.6	0.4	0.4999	0.3051	0.0036	0.0050	0.2857	0.0107	0.3065	0.0895	0.0856
0.5	0.5	0.5007	0.2534	0.0058	None	0.2374	0.0074	0.2513	0.1113	0.1100
0.3	0.7	0.5004	0.1501	0.0102	*	0.1365	0.0019	0.1488	0.1610	0.1608

* Not determined.

The results of the thermal and roentgenostructural analysis uniquely indicates the formation of compounds between V_2O_5 and K_2SO_4.

The composition of this compound, evidently, does not correspond to a simple 1 to 1 relationship, but lies very close to it in the direction of being more rich in V_2O_5. This thesis is confirmed by the high-temperature thermal effects in fusion cakes with 0.5 and 0.6 mole-portions of V_2O_5. In the first it is found at 490°, and in the second at 520°. Roentgenographically this was confirmed by the fact that on the powder roentgenogram of a fusion cake with 0.5 mole-portion of V_2O_5, there is present a weakly-expressed maximally-intense K_2SO_4 line. It is possible, however, that the compound being formed corresponds in composition to $V_2O_5 \cdot K_2SO_4$, but the observed phenomena are evoked by the absence of complete internal equilibrium.

The endothermically formed compound is not stable and is readily decomposed. During the leaching of the fusion cakes, ground to a powder, with water, their sulfate portion is entirely extracted with water along with a very small quantity of vanadium oxide, of which the water-insoluble residue is entirely composed Both in the water extract and in the insoluble residue along with V_2O_5 there was also detected a lower form of vanadium oxide — — V_2O_4, absent in the pure starting preparation, which indicates the partial formation of potassium vanadico-vanadate. The formation of these compounds ($V_2O_4 \cdot 5V_2O_5 \cdot K_2O$, $V_2O_4 \cdot 4V_2O_5 \cdot K_2O$ and others) was observed by Prandtl and Murschhauser [10] and Canneri [11] during the crystallization of fusion cakes of vanadium pentoxide with alkalis at a ratio $V_2O_5 : K_2O > 1$. It is not without interest to note that the color of the fusion cakes formed is considerably darker than that of solidified fused V_2O_5. The darkest color was in the fusion cake with 0.5 mole-portion of V_2O_5. The fusion cakes ground to powder had an intense brownish-olive color, markedly different from the color of ground vanadium pentoxide. The results of the chemical analyses are set forth in Table 1. It should be noted that both the boiling and the subsequent treatment of the insoluble portion with sodium hydroxide were conducted in a stream of nitrogen bubbled through liquid placed in a flask with a ground top. The total results of the thermal and roentgenostructural investigations permit us to construct a diagram of the composition of the system $V_2O_5-K_2SO_4$ (Fig. 4).

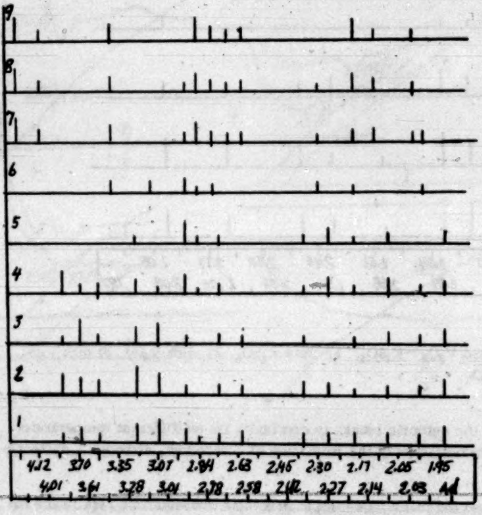

Fig. 3. Roentgenogram chart of the system $V_2O_5-K_2S_2O_7$.
1) Pure $K_2S_2O_7$; 2) 10% V_2O_5; 3) 20% V_2O_5; 4) 30% V_2O_5; 5) 40% V_2O_5; 6) 50% V_2O_5; 7) 60% V_2O_5; 8) 70% V_2O_5; 9) pure V_2O_5.

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* Not determined.

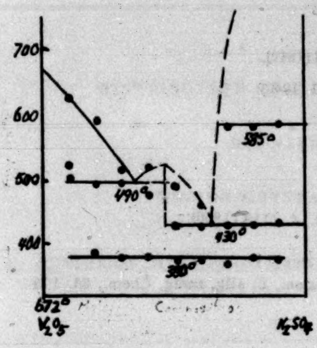

Fig. 4. Fusion curve of the system $V_2O_5-K_2SO_4$.

The system $V_2O_5-K_2S_2O_7$. Thermal investigations of the system $V_2O_5-K_2S_2O_7$ according to the cooling curves did not permit the presence of heat effects to be established in the region of mixtures containing less than 0.5 mole-portions of V_2O_5. This depended on its capacity to form glass readily.

A larger number of effects was detected on the heating curves. At a temperature close to 222° an endothermic effect is observed which depends on the polymorphic conversion of potassium pyrosulfate. At a temperature of the order of 272° an exothermic effect is observed which reaches a maximum at the ratio $V_2O_5 : K_2S_2O_7 = 1:1$. On the cooling curve and on the repeated heating curve it is absent over all the interval of composition. Evidently, the maximum is linked with the formation of a compound of possible composition $V_2O_5 \cdot K_2S_2O_7$.

In connection with the fact that equilibrium is not completely established, unreacted pyrosulfate is present in the form of a separate phase and evokes an endothermic effect. The latter is increased in proportion to the increase of $K_2S_2O_7$ content, which is linked with the second polymorphic conversion of this component at 350°. The curves corresponding to compositions containing more than 0.4 mole-portion of V_2O_5, show the presence of one more endothermic effect, the position of which is displaced from 668° in pure V_2O_5 to 556° in mixtures containing 0.6 mole-portions of this component. These are the only effects displayed on the cooling curves. They may be interpreted as associated with the liquidus lines.

TABLE 2

Composition of the fusion cake		Amount of weighed sample (in g)	Theoretical content of V_2O_5	Aqueous extract		Residue		Total content calculated as V_2O_5	Content of SO_3	
V_2O_5(in moles)	$K_2S_2O_7$(in moles)			V_2O_5	V_2O_4	V_2O_5	V_2O_4		Theoretical	In the aqueous extract
0.7	0.3	0.4995	0.3123	0.0107	None	0.2914	0.0021	0.3044	0.1178	0.1155
0.3	0.7	0.4999	0.1172	0.0139	0.0042	0.0981	0.0017	0.1185	0.2408	0.2387

The increased tendency of melts containing potassium pyrosulfate to vitrify extraordinarily complicates the roentgenographic investigation. All the roentgenograms of the mixtures are strongly fogged which does not permit definite conclusions to be made regarding the origin of certain lines of the roentgenogram. A significant change in the comparative intensity of the diffraction lines on the roentgenograms of the fusion cakes rich in potassium pyrosulfate, is to be explained, evidently, by the partial hydration under the action of the water vapor of the air during the preparation of the samples for exposure, which leads to the formation of $KHSO_4$ (Fig. 3).

It is necessary to note that the compound formed during the leaching with water is also unstable, similarly to what was observed in the sulfate system (Table 2).

SUMMARY

1. Thermographic and roentgenographic investigations of the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$ were conducted.

2. In the system $V_2O_5-K_2SO_4$, the formation of a compound was detected, close in composition to $V_2O_5 \cdot K_2SO_4$, with a melting point around 500°. The eutectic point between this compound and potassium sulfate lies below 430° and corresponds to an approximate content of V_2O_5 of 0.4 mole-portion. An approximate composition diagram was constructed for this system.

3. In the system $V_2O_5-K_2S_2O_7$, melts with a great content of pyrosulfate (above 0.4 mole-portion) possessed low melting points and readily vitrified during cooling. During heating of mixtures of V_2O_5 and $K_2S_2O_7$, an exothermic effect was detected at 275°, which can be explained by the formation of the compound $V_2O_5 \cdot K_2S_2O_7$.

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DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN THE SOLID AND LIQUID PHASES DURING CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

II. EQUILIBRIUM IN CERTAIN SYSTEMS WITH SCHOENITE (PICROMERITE) TYPE DOUBLE SALT COMPONENTS

G. I. Gorshtein and N. I. Silantyeva

Equilibrium in the System $CoSO_4 \cdot (NH_4)_2SO_4 - NiSO_4 \cdot (NH_4)_2SO_4 - H_2O$ at 20°

Double salts of the schoenite type ($MgSO_4K_2SO_4 \cdot 6H_2O$, where in place of Mg there may be Co^{++}, Ni^{++}, Fe^{++}, Zn^{++}, Cu^{++}, Mn^{++}, Cd^{++}, in place of K – NH_4^+, Rb^+, Cs^+, Tl^+, in place of S – Se, Te, Cr) are usually truly isomorphic and form a continuous series of solid solutions. Accordingly, the study of systems with these components presents considerable interest for the elucidation of the laws governing the distribution of isomorphic components between the solid and liquid phases.

In the investigation of the system $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ the concentrations of cobalt in the crystals and in the mother liquors were determined by means of potentiometric titrations with potassium ferricyanide in an ammoniacal medium. The concentration of nickel was determined gravimetrically by means of precipitation with dimethylglyoxime. At low nickel concentrations, the nickel was preliminarily isolated as the solid dimethylglyoxime by the method of Peshkova [2].

The results of the experiments are given in Table 1 and in Figure 1 (the equilibrium composition diagram) and Figure 2 (the distribution diagram).

TABLE 1

Equilibrium in the System $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20° [I – % $CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis				II		Distribution coefficient	
	of the solid phase		of the mother liquor		in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Co)	$D_{equilibrium}$ (Co, Ni)
	I	II	I	II				
1			16.70	0	0	0	–	–
2	88.14	8.58	15.66	0.47	8.91	2.9	3.3	0.30
3a	84.20	13.32	15.22	0.71	13.7	4.5	3.5	0.29
3b	82.83	13.04	15.08	0.68	13.7	4.3	3.5	0.29
4a	76.04	21.08	14.05	1.19	21.8	7.8	3.3	0.30
4b	76.86	21.37	13.97	1.16	22.0	7.65	3.5	0.29
5	57.17	37.28	10.31	2.30	39.6	18.2	3.0	0.34
6a	21.80	74.20	4.82	5.19	77.4	51.9	3.2	0.31
6b	20.60	73.40	4.11	5.35	78.2	56.6	2.8	0.36
7a	13.64	80.67	3.30	5.68	85.7	63.3	3.4	0.29
7b	13.37	81.56	3.28	5.69	85.5	63.4	3.4	0.29
8a	7.82	89.85	1.97	7.16	92.0	78.5	3.2	0.31
8b	7.82	84.10	1.97	7.34	91.4	78.8	2.9	0.34
9a	6.03	88.66	1.55	7.38	93.7	82.6	3.1	0.32
9b	6.77	87.69	1.61	7.40	93.6	82.1	3.1	0.32
10.			0	8.45	100.00	100.00	–	–

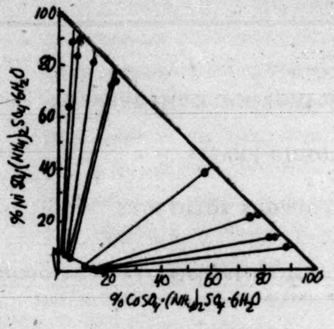

Fig. 1. Equilibrium composition diagram for the system $NiSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°.

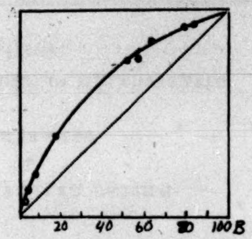

Fig. 2. Distribution diagram for the system $NiSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°. A) % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor.

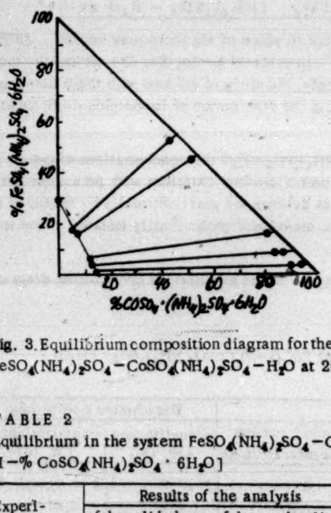

Fig. 3. Equilibrium composition diagram for the system $FeSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°.

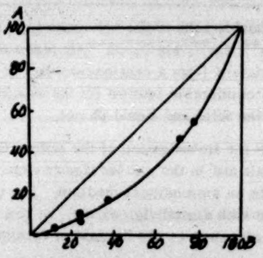

Fig. 4. Distribution diagram for the system $FeSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°. A) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor

TABLE 2

Equilibrium in the system $FeSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°. [I – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis				I		Distribution coefficient	
	of the solid phase		of the mother liquor		in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Fe, Co)	$D_{equilibrium}$ (Co, Fe)
	I	II	I	II				
			0	16.70				
1a	4.04	94.02	1.89	14.08	4.09	11.83	0.318	3.14
1b	3.89	89.51	1.89	14.02	4.06	11.87	0.315	3.17
2a	9.43	86.67	4.29	13.26	9.68	23.91	0.336	2.97
2b	9.21	83.84	4.29	13.26	9.66	23.91	0.331	3.02
3a	16.08	80.92	6.94	11.90	16.44	36.83	0.330	3.03
3b	14.91	78.37	6.92	11.92	15.64	36.83	0.319	3.13
4a	44.88	50.75	16.60	6.02	46.56	73.38	0.315	3.17
4b	44.47	51.03	16.47	5.83	46.18	73.81	0.317	3.15
5a	52.13	43.98	18.37	4.99	53.92	78.63	0.318	3.14
5b	52.29	44.06	18.41	5.03	54.22	78.53	0.330	3.03
			28.75	0				

TABLE 3

Equilibrium in the System $NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ at 20°. [I – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis						Total degree of crystallization, a	II		Distribution coefficient	
	of the solid phase		of the mother liquor		starting solution			in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Fe)	$D_{equilibrium}$ (Fe, Ni)
	I	II	I	II	I	II					
			0	28.75							
1a	10.54	83.80	0.26	26.70	1.30	32.5	0.28	88.5	99.0	13.2	0.076
1b	10.91	86.30	0.26	26.60	1.30	32.5	0.28	88.7	99.0	12.8	0.078
2a	19.90	76.79	0.54	24.79	3.0	29.6	0.27	79.2	98.0	12.1	0.083
2b	19.60	76.30	0.54	24.79	3.0	29.6	0.27	79.4	98.0	11.9	0.084
3a	30.40	66.47	0.86	22.61	4.39	28.59	0.38	69.6	96.3	12.0	0.083
3b	29.50	65.64	0.84	22.79	4.39	28.59	0.37	70.5	96.4	11.6	0.086
4a	49.50	43.92	1.68	17.50	7.19	20.79	0.38	46.1	91.2	12.1	0.083
4b	50.94	44.70	1.69	17.49	7.19	20.79	0.38	46.1	91.1	11.7	0.085
5a	60.74	34.05	2.13	14.70	14.06	1.13	0.49	35.2	86.9	11.3	0.081
5b	59.30	34.28	2.20	14.14	14.06	1.13	0.49	35.4	86.5	11.6	0.086
6a	74.17	20.68	3.66	9.76	13.96	11.47	0.55	21.5	72.7	10.0	0.10
6b	73.63	20.71	3.65	9.53	13.96	11.47	0.55	22.4	72.3	10.0	0.10
7a	76.63	18.26	3.70	8.96	12.20	10.18	0.50	18.8	70.8	10.43	0.096
7b	73.63	18.66	3.86	8.81	12.20	10.18	0.49	19.6	69.5	9.38	0.11
10a	81.08	14.30	4.42	7.37	9.11	8.11	0.36	14.66	62.5	9.85	0.10
10b	78.55	13.70	4.48	7.75	9.11	8.11	0.33	14.22	63.3	10.40	0.096
11a	81.69	12.59	4.49	6.49	10.14	7.02	0.34	13.00	59.2	10.0	0.10
11b	81.72	12.58	4.47	6.49	10.14	7.02	0.34	13.98	59.2	10.0	0.10
12a	85.77	9.69	5.68	5.33	–	–	–	10.00	48.4	8.33	0.12
12b	86.22	9.81	5.69	5.31	–	–	–	10.11	48.2	8.33	0.12
13a	85.82	6.33	6.38	3.60	22.56	4.08	0.67	6.59	36.1	7.69	0.13
13b	87.84	6.14	6.34	3.62	22.56	4.08	0.68	6.32	36.3	8.33	0.12
14a	91.93	5.32	6.32	2.87	16.7	3.11	0.59	5.40	31.2	8.33	0.12
14b	91.76	5.47	6.34	2.88	16.7	3.11	0.59	5.50	31.2	7.69	0.13
15a	93.22	3.64	7.56	2.10	12.94	2.23	0.40	3.75	21.7	7.14	0.14
15b	90.70	3.70	7.53	2.12	12.94	2.23	0.40	3.80	22.0	7.14	0.14
16a	94.70	2.02	7.45	1.04	14.06	1.13	0.48	2.05	12.3	7.14	0.14
16b	94.10	1.96	7.50	1.05	14.06	1.13	0.47	2.00	12.2	7.14	0.14
			8.45								

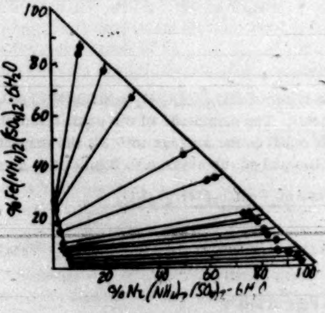

Fig. 5. Equilibrium composition diagram for the system $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20°.

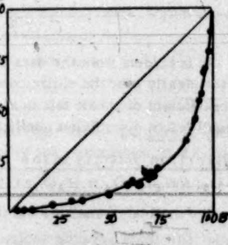

Fig. 6. Distribution diagram for the system $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20°. A) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor.

TABLE 4

Equilibrium in the System $NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ at 0°. [I – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis						Total degree of crystallization, a	II		Distribution coefficient	
	of the solid phase		of the mother liquor		starting solution			in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Fe)	$D_{equilibrium}$ (Fe, Ni)
	I	II	I	II	I	II					
33a	15.39	71.58	0.30	18.00	1.87	28.93	0.38	82.61	98.35	12.5	0.080
33b	16.34	75.73	0.33	18.20			0.37	81.96	98.21	12.1	0.082
30a	26.07	67.53	0.57	16.53	3.53	22.44	0.52	71.40	96.66	11.5	0.086
30b	26.80	69.91	0.49	15.83			0.55	71.99	96.99	12.6	0.079
31a	32.78	57.41	0.73	13.91	2.62	17.17	0.30	62.92	95.08	11.2	0.089
31b	33.97	59.13	0.76	14.53			0.27	59.96	95.04	12.7	0.078
32a	55.20	40.21	1.19	10.90	3.87	12.46	0.29	41.80	90.16	12.7	0.078
32b	54.97	41.05	1.20	10.87			0.30	42.47	90.05	12.1	0.083
45a	82.24	11.66	2.94	4.33	7.35	4.73	0.44	12.10	59.56	10.7	0.093
45b	84.89	12.29	2.92	4.26			0.45	12.54	59.33	10.2	0.098
43a	84.29	10.11	3.31	3.34	7.97	3.79	0.46	10.56	50.22	8.5	0.12
43b	82.11	9.89	3.31	3.41			0.46	10.47	50.74	8.8	0.11
42a	87.59	7.23	3.25	2.54	8.93	2.69	0.53	7.50	43.87	9.7	0.10
42b	85.93	7.32	3.76	2.62			0.48	7.68	41.06	8.4	0.12
40a	87.20	4.44	4.36	1.65	8.16	1.77	0.42	4.71	27.45	7.7	0.13
40b	90.76	4.52	4.68	1.61			0.39	4.67	25.60	7.1	0.14

TABLE 5

Values of the equilibrium distribution coefficients according to the experimental data of Hill [3]

1	2		3		
Per cent of Ni salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Zn)	Per cent of Ni salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Cu)	Per cent of Zn salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Zn, Cu)
14.1	3.6	3.9	12.0	14.0	2.5
14.0	3.9	3.9	12.9	13.4	2.8
20.6	3.9	5.5	16.6	25.7	2.7
28.3	3.9	5.6	16.7	25.7	2.7
27.3	4.4	10.3	15.7	46.5	4.0
43.5	5.7	10.0	16.7	46.5	4.0
42.4	5.8	22.0	17.8	68.0	9.2
74.0	2.9	21.5	20.0	68.0	12.7
		51.5	13.0		
		51.5	13.6		

As is evident from the data of the last column of Table 1, the system $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ behaves ideally over the entire concentration range of both components. The magnitude of the equilibrium distribution coefficient of cobalt salt in nickel salt $D_{equilibrium\ (Co,\ Ni)}$ is equal on the average to 0.31; the magnitude of the equilibrium distribution coefficient of nickel salt in cobalt salt is equal on the average to 3.2.

Equilibrium Distribution of Components in the System $FeSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°

The method of analysis was the same as that employed in the investigations of the system $CoSO_4 - FeSO_4 - H_2O$ [1].

The results of the experiments are set forth in Table 2 and in Figs. 3 and 4.

The system $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O - CoSO_4(NH_4)_2SO_4 \cdot 6H_2O - H_2O$ at 20° can be considered ideal over the entire concentration range of the components. The average magnitude of the equilibrium distribution coefficient of iron salt in relation to cobalt salt $D_{equilibrium\ (Fe,Co)}$ is equal to 0.32; the opposite average magnitude of the equilibrium distribution coefficient of cobalt salt in relation to iron salt $D_{\text{equilibrium (Co,Fe)}}$ is equal to 3.1.

Equilibrium in the System $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20°.

The method of analysis employed was the same as in the investigation of the system $FeSO_4 - NiSO_4 - H_2O$ [1]. The results of the experiments are set forth in Table 3 and in Figs. 5 and 6.

This system, in contrast to the two preceding, was not ideal over the entire range of concentrations of the components.

The magnitude of the equilibrium distribution coefficient of nickel salt in the iron salt $D_{\text{equilibrium (Ni, Fe)}}$ varied from 7.1 to 13 and on the average was equal to 10.1; in view of this the system can be considered ideal only within a limited concentration range at the edges of the distribution diagram.

In one of these intervals the magnitude of $D_{\text{equilibrium (Ni, Fe)}}$ retains a value in the range 12-13, during the change in the concentrations of nickel salt in the salt portion of the mother liquor of from 0 to 15%, and accordingly in the solid phase of from 0 to 35%. At the other edge of the diagram the magnitude of the equilibrium distribution coefficient of iron in the nickel salt $D_{\text{equilibrium (Fe, Ni)}}$ retains values in the limits 0.13-0.14, at concentrations of iron salts in the salt portion of the mother liquor of from 0 to 30% or, accordingly, in the solid phase of from 0 to ~5%.

Equilibrium in the System $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 0°.

The results of the experiments are set forth in Table 4.

The equilibrium distribution of components at 0° has exactly the same character as at 20°.

DISCUSSION OF RESULTS

Hill [3] and others studied the equilibrium distribution of isomorphic components in a number of systems with salts of the schoenite (picromerite) type at a temperature of 25°. They advanced the general proposition that such systems are not ideal and that the value of $D_{\text{equilibrium}}$ for them is unilaterally changed by increase in the concentration of one of the components from 0 to 100%.

This conclusion was hardly substantiated, however, by the experimental data of these investigators.

As an illustration we present (Table 5) the values of the equilibrium distribution coefficients calculated by us from the data of Hill and co-workers for three of the systems which they studied:

1. $ZnSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$.
2. $CuSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$.
3. $CuSO_4(NH_4)_2SO_4 - ZnSO_4(NH_4)_2SO_4 - H_2O$.

The considerable and irregular dispersion of the values of $D_{\text{equilibrium}}$ in these systems in conjunction with the small number of points indicates the inadequate reliability of the data of these authors.

Our investigations, in contrast to the general hypothesis of Hill and co-workers, have established that the systems $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ and $CoSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ with components of the schoenite (picromerite) type are ideal at 20° over the entire range of concentration of components. Deviations from the mean values of $D_{\text{equilibrium}}$ in our data on the average did not exceed ± 5% relatively, which simultaneously serves as confirmation of the reliability of the methods of investigation employed by us.

Deviations from the ideal for the system

$$NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$$

are evidently associated with very significant difference in the solubility of both salts, which possibly evokes in its turn a more acute difference in the magnitudes of the coefficients of activity of the components in the liquid and solid phases.

The changes in the magnitudes of $D_{\text{equilibrium}}$ have a smooth character.

Although one of the three systems investigated by us exhibits certain deviations from the ideal, the mean values of the equilibrium distribution coefficients for these systems satisfy the formula presented in [1]: $D_{\text{equilibrium (A, C)}} = D_{\text{equilibrium(A, B)}} \cdot D_{\text{equilibrium(B, C)}}$. Actually, $D_{\text{equilibrium (Ni, Co)}} = 3.3$, $D_{\text{equilibrium (Co,Fe)}} = 3.1$; hence $D_{\text{equilibrium (Ni, Fe)}}$ is determined by calculation $3.3 \cdot 3.1 = 10.2$, as contrasted with a mean value 10.0 obtained from the experimental data.

The dependence between the concentrations of the components in the equilibrium mother liquors is expressed in a tetragonal diagram for the two ideal systems as a straight line. For the third system: $NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ this relationship has a more complex character.

SUMMARY

1. The equilibrium at 20° in the systems:

$$CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$$
$$CoSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$$

and in the system $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20° and 0° was studied.

2. It was established that the first two systems are ideal at 20° over the entire range of concentrations of both isomorphic components. The following values for the equilibrium distribution coefficients were found: for the system: double salt of nickel – double salt of cobalt – water $D_{\text{equilibrium}(Ni, Co)} = 3.2$, $D_{\text{equilibrium}(Co, Ni)} = 0.31$; for the system: double salt of cobalt – double salt of iron – water $D_{\text{equilibrium}(Co, Fe)} = 3.1$, $D_{\text{equilibrium}(Fe, Co)} = 0.32$.

3. It was found that the system $NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ is not ideal at 20° over the entire concentration range, but only in fixed limits at the edges of the equilibrium diagram. The value of the equilibrium distribution coefficient for admixture of Ni during the crystallization of the double salt of iron amounts at 20° and at 0° to 12.5; the value of the equilibrium distribution coefficient for Fe^{++} admixture during the crystallization of the double salt of nickel amounts to 0.14 at 20° and at 0°.

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* See Consultants Bureau Translation, page 1355.

INVESTIGATION OF COMPLEX FORMATION BETWEEN THE BISMUTH ION AND THE IONS OF TARTARIC ACID

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The ions of tartaric and citric acids can form complex compounds with the ions of bismuth which are water soluble at all pH values.

The data in the literature concerning the composition of these complex compounds are rather contradictory [1-5]. In addition, in the majority of the indicated cases the composition of the tartaric and citric complexes was considered without taking into account the pH of the medium, although the content of tartaric acid ions and the hydrolysis of bismuth salts is determined by the pH value of the medium.

The object of the present investigation was the study of the chemistry of the complex-formation reactions of the Bi^{3+} ion with the ions of tartaric acid, taking into account the influence of the pH of the medium by a potentiometric method, in order to establish the composition of the complex ions and to calculate the instability constants of these complex ions. Chemically pure metallic bismuth was taken as the recording electrode and a saturated calomel electrode was used as the standard. The measurements were conducted on a potentiometer of the Rapps type.

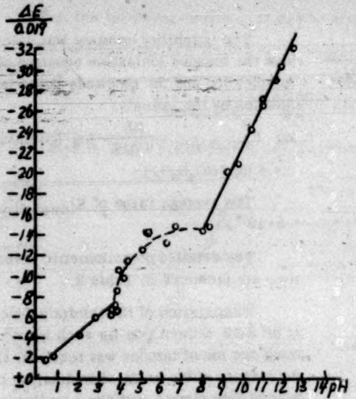

Fig. 1. The potential of a bismuth electrode as a function of the pH at $[Bi^{+3}]$ = 0.01 mole/liter and of $Na_2C_4H_4O_6$ = 0.2 mole/liter.

The investigation of the dependence of the potential of the bismuth electrode on the pH of the medium at a constant concentration of $[Bi^{+3}]$ of 0.01 mole/liter and of $Na_2C_4H_4O_6$ of 0.2 mole/liter is presented in Fig. 1.

It is evident from the data of Fig. 1 that there are 3 clearly expressed zones: the first – in the acid region at pH 1-4 is characterized by rectilinear dependence of the electrode potential on pH; in the second – at pH ≈ 4-9 a rectilinear dependence of the electrode potential on pH is not observed; the third zone – in alkaline media at pH ≈ 9-13.5 is characterized by a rectilinear dependence of the electrode potential on the pH of the medium.

Taking into account the acid-base nature of the bismuth ion, which has the capacity to undergo hydrolysis at pH 2-3, and the peculiarities of tartaric acid, in which the first ionization constant is of the order of $K_1 = 1 \cdot 10^{-3}$ and the second $K_2 = 9 \cdot 10^{-5}$, it is natural to suppose that a reciprocal reaction of the bismuth ion with the bitartrate ion proceeds in the first zone and that a reciprocal reaction of the bismuth ion with tartrate and hydroxyl ions proceeds in the third zone. The second zone appears to be an intermediate region where formation of basic bismuth salts of indeterminate composition is possible. In this zone, i.e., at pH 4-8, if the concentration of sodium tartrate is less than 0.1 mole/liter, and $[Bi^{+3}]$ = 0.01 mole/liter, the precipitation of a white amorphous precipitate is observed. The chemical analysis of this precipitate showed that it consisted of a mixture of $Bi(OH)_3$ with tartrate, i.e., of basic bismuth salt and tartaric acid.

The first and third zones were of interest for the potentiometric method and were carefully studied to elucidate the chemical composition of the compounds obtained in solution and to calculate the ionization constants of these compounds.

In the first zone, i.e., in the region of low pH values, reciprocal reaction of bismuth ions with bitartrate ions should occur. The potential values of the bismuth electrode as a function of the concentration of the bitartrate ion are presented in Fig. 2.

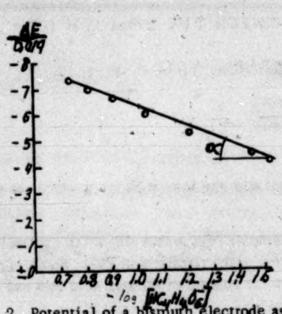

Fig. 2. Potential of a bismuth electrode as a function of the concentration of $HC_4H_4O_6^{-1}$ at pH 2.62 and $[Bi^{+3}] = 0.01$ mole/liter.

It is evident from the data of Fig. 2 that the tangent of the angle of inclination of the straight line plotted with the coordinates $\frac{\Delta E}{0.019} - \log [HC_4H_4O_6^-]$, exhibits the coordination number of the bismuth ion with reference to the bitartrate ion; in the given case equal to 4.1, i.e., close to 4. Consequently, 1 ion of bismuth coordinates 4 ions of bitartrate. The bitartrate ion was titrated with a solution of bismuth nitrate at pH 2-3 to verify these data. The appearance of stable turbidity formed as a result of the hydrolysis of bismuth nitrate (Table 1) served as indicator.

It is evident from column 5 of Table 1 that at pH 2.4-2.9 the ratio $\frac{[HC_4H_4O_6^-]}{[Bi^{+3}]} \approx 4$.

Thus, the results of visual titration are confirmed by the data of the potentiometric investigation. On the basis of these data one can assert that at pH 2-3 the bismuth ion forms a complex ion with the bitartrate ion of composition $Bi(HC_4H_4O_6)_4^{-1}$, and the instability constant of this complex ion (concentrated is expressed by the equation:

$$K_{instability_1} = \frac{[Bi^{+3}]\,[HC_4H_4O_6^{-1}]}{[Bi(HC_4H_4O_6)_4^{-1}]}.$$

TABLE 1

Amount of 0.5 mole/liter of $Na_2C_4H_4O_6$ taken	Amount of 0.1 mole/liter of $Bi(NO_3)_3$ (in ml) consumed	pH of the final solution	Amount of $HC_4H_4O_6^-$ contained in m. moles	$\frac{HC_4H_4O_6^-}{[Bi^{+3}]}$
5.00	1.20	2.40	0.515	4.3
5.0	1.80	2.65	0.784	4.3
5.0	2.10	2.68	0.821	3.9
2.0	0.91	2.77	0.372	4.0
4.0	1.83	2.77	0.744	4.0
5.0	2.60	2.82	1.000	3.8
2.0	1.06	2.88	0.427	4.0
2.0	1.05	2.88	0.427	4.0
2.0	1.06	2.90	0.435	4.1
4.0	2.6	3.92	0.675	2.6
5.0	2.0	4.72	0.436	2.2
5.0	1.4	5.29	0.135	0.96

The instability constant was calculated from the reduced ionization equation of the complex ion and the electrode potential equation by the formula:

$$\log K_{instability_1} = \frac{\Delta E}{0.019} - \log [complex] + 4 \log [HC_4H_4O_6^-].$$

The average value of $K_{instability_1} = 5 \cdot 10^{-9}$.

The detailed potentiometric investigations are presented in Table 2.

Investigation of the third (alkaline) zone at pH 8-13, showed that for each ion of bismuth one ion of tartrate was required, since the tangent of the angle of inclination of the straight line plotted with the coordinates $\frac{\Delta E}{0.019} - \log(C_4H_4O_6^{-2})$, was equal to 1.

TABLE 2

$[Bi^{+3}]$ (in mole/liter	$Na_2C_4H_4O_6$ (in mole/liter)	pH	e.m.f. (in volts)	$\frac{\Delta e.m.f.}{0.019}$	$[HC_4H_4O_6^-]$ (in mole/liter)	$K_{instability_1}$
0.01	0	1.1	0.025	—	–	–
0.01	0.10	2.62	0.106	−4.26	0.0299	$4.36 \cdot 10^{-9}$
0.01	0.20	2.62	0.125	−5.26	0.0598	$7.08 \cdot 10^{-9}$
0.01	0.30	2.62	0.140	−6.05	0.0897	$5.7 \cdot 10^{-9}$
0.01	0.40	2.63	0.152	−6.70	0.1196	$4.1 \cdot 10^{-9}$
0.01	0.50	2.62	0.160	−7.10	0.1495	$4.0 \cdot 10^{-9}$
0.01	0.60	2.62	0.1648	−7.37	0.1794	$4.5 \cdot 10^{-9}$

Visual titration of the tartrate ion with $Bi(NO_3)_3$ solution at pH 13 showed that for 0.25 ml of 1 mole/liter $Na_2C_4H_4O_6$, 2.5 ml of 0.1 mole/liter of $Bi(NO_3)_3$ were consumed, which gives the ratio $[C_4H_4O_6^{-2}]/[Bi^{+3}] = 1$.

TABLE 3

Concentration of Bi^{+3} = 0.01 mole/liter

$K_2C_4H_4O_2$ (in mole/ liter)	pH	e.m.f. (saturated calomel electrode) (in volts)	$\frac{\Delta e.m.f.}{0.019}$	$K_{instability_2}$
0	1.1	0.025	—	—
0.10	10.0	0.4043	−19.95	$1.1 \cdot 10^{-31}$
0.10	11.25	0.4810	−24.00	$0.56 \cdot 10^{-31}$
0.10	11.9	0.4970	−24.84	$7.2 \cdot 10^{-31}$
0.10	12.83	0.5410	−27.16	$2.14 \cdot 10^{-31}$
0.10	13.40	0.610	−30.80	$0.25 \cdot 10^{-31}$

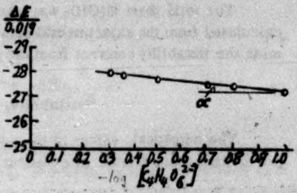

Fig. 3. Potential of a bismuth electrode as a function of the concentration of $[C_4H_4O_6^{-2}]$ at pH 13 and $[Bi^{+3}]$ = 0.01 mole/liter; tan α = 1.

Consequently, 1 ion of tartrate is required for 1 ion of bismuth in alkaline medium. In addition to the tartrate ion the OH' ion can react with the bismuth ion in alkaline medium. This follows from Table 3 and Figs. 1 and 4, in which the bismuth potential measurements are presented as a function of the pH of the solution.

It follows from the potentiometric determinations (Fig. 4) that 1 ion of bismuth coordinates 3 OH' ions in the alkaline tartrate complex.

Thus, the following composition can be assigned to this complex ion: $[Bi(OH)_3C_4H_4O_6]^{-2}$.

The results of the calculation of the instability constants according to the potentiometric investigations and the formula:

$$\log K_{instability_2} = \frac{\Delta e.m.f.}{0.019} - \log\ [complex] + \log[C_4H_4O_6^{-2}] + 3pH - 3pK_W$$

are presented in Table 3. The mean value of the instability constant is of the order of 10^{-31}.

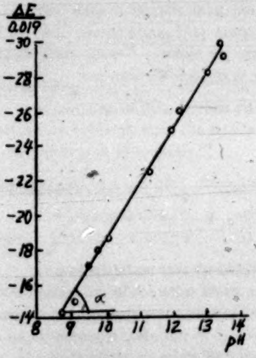

Fig. 4. Potential of a bismuth electrode as a function of pH at a concentration of $K_2C_4H_4O_6$ equal to 0.1 mole/liter, and of Bi^{+3} = 0.01 mole/liter; tan α = 3.0.

TABLE 4

$Na_2C_4H_4O_5$ (in mole/ liter)	Bi (in g/50 ml)	[complex] (in mole/ liter)	$K_{equilibrium}$
0.01	0.04	0.004	0.40
0.03	0.102	0.010	0.33
0.05	0.166	0.016	0.32
0.08	0.272	0.026	0.32
0.10	0.296	0.028	0.28
0.10	0.296	0.028	0.28
		Mean	0.32

Having established the composition of the alkaline tartrate complex ion of bismuth and having calculated its ionization constant from the potentiometric data, starting from the solubility product of hydrated bismuth oxide $K_{s\ Bi(OH)_3} = 4.3 \cdot 10^{-31}$, we attempted to verify the value of the instability constant by the solubility method. The investigations essentially consisted in treating the solid phase $Bi(OH)_3$ in a constant assigned alkali concentration with a solution of sodium tartrate with its concentration varying according to changes in the concentration of $Na_2C_4H_4O_6$ determined in a bismuth solution (by electrolysis).

We further assumed that the following complex-formation reaction occurred:

$$Bi(OH)_3 + C_4H_4O_6^{-2} \rightleftarrows [Bi(OH)_3C_4H_4O_6]^{-2}.$$

The equilibrium constant of this reaction is expressed by the equation:

$$K_{\text{equilibrium}} = \frac{[\text{complex}]}{[C_4H_4O_6^{-2}]}.$$

The solid phase $Bi(OH)_3$ was taken as a constant quantity and always occurred in excess. $K_{\text{equilibrium}}$ was calculated from the experimental data (Table 4). Knowing the value of the latter and $K_{S\ Bi(OH)_3}$, one can determine the instability constant from the equation:

$$K_{\text{instability}_2} = \frac{K_{S\ Bi(OH)_3}}{K_{\text{equilibrium}}} = \frac{4.3 \cdot 10^{-31}}{0.32} = 13.4 \cdot 10^{-31}.$$

The numerical values of the instability constants of the alkaline tartrate complex of bismuth obtained by the two distinct methods were in excellent agreement.

SUMMARY

Depending on the pH of the medium, the bismuth ion gives two complex compounds with the ions of tartaric acid: 1) in acidic medium at pH $\approx$ 2-3, the complex ion $Bi(HC_4H_4O_6)_4^{-1}$ with a $K_{\text{instability}} = 10^{-9}$ and 2) in alkaline medium at pH $\approx$ 9-14 the complex ion $[Bi(OH)_3C_4H_4O_6]^{-2}$ with a $K_{\text{instability}} = 10^{-31}$.

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* See Consultants Bureau Translation, page 1977.

THE THERMODYNAMICS OF OXIDE PHASES OF VARIABLE COMPOSITION

I. THE THERMODYNAMICS OF FERROUS OXIDE

S. M. Ariya, M. P. Morozova and L. A. Shneider

It is generally known that the subgroup elements have a characteristic capacity to form oxides of variable composition. This phenomenon has practical as well as theoretical significance. However, although we already have available a detailed enough structural formula for the phase of variable composition, and in a number of cases know with sufficient precision the extent of the region of homogeneity of many elements, the laws governing the changes in the extent of the region of homogeneity of oxides during the transition from one element to another are still not clear.

It is natural that before this question will be reconciled with the positions of the periodic law and the theory of the chemical bond, similar compounds, the bertollides of N. S. Kurnakov, must be studied not only structurally but also thermodynamically. However, up to the present time, such thermodynamical investigation of oxide phases of variable composition is almost wholly lacking.

The simplest way to acquire an understanding of the thermodynamics of oxides of variable composition appears to be the study of their equilibria (at variable composition) with gaseous oxidizing-reducing systems.

The present work is one of the links in a proposed chain of investigations devoted to the thermodynamics of ferrous oxide.

As is well known, ferrous oxide is thermodynamically stable only above 572°; in the opinion of the majority of authors [1], the stoichiometric phase – FeO – is metastable at all temperatures, while the thermodynamically stable phase has the composition FeO_{1+x}, where x depends both on the temperature and on the pressure of oxygen in the gaseous phase which coexists with ferrous oxide.

The work of Darken and Garri [2] was devoted to determination of the enthalpies of formation of ferrous oxides of variable composition; they investigated the equilibrium of ferrous oxide with CO_2/CO mixtures, but at an adverse temperature range*, in which the entire region of homogeneity of ferrous oxide corresponded to a change in the ratio P_{CO_2}/P_{CO} of several hundredths at an absolute value of around 0.3 for this ratio.

In addition to this, Darken and Garri obtained data for the magnitude of the region of homogeneity which were noticeably different from the results of the investigations of other authors, which compels one to treat their data with a certain degree of caution.**

Investigation of the Equilibrium $FeO_{1+x+y} + yCO \rightleftarrows FeO_{1+x} + yCO_2$

Ferrous oxide containing, according to the spectral analysis data, the following admixture: Ni, Co ~ 0.001, Mn < 0.001, Cu ~ 0.001, V ~ 0.001, Cr, W < 0.01%, served as the object of the investigation.

The equilibrium was investigated at 1104 and 1182°K in a circulation apparatus (delivery of gas 5 liters/hour); the composition of the solid phase was established with the use of spring scales. The gaseous mixture at the attainment of equilibrium was analyzed, as usual, by absorption of carbon dioxide gas by alkali, and of carbon monoxide in an ammoniacal solution of Cu_2Cl_2. Particular attention was paid to maintaining constant temperature: with the use of a phototitration relay the temperature was kept constant with a precision of ± 0.2°. The observed dependence of the composition of the solid phase on the ratio of the partial pressure of carbon dioxide to carbon monoxide is given in Table 1 and in Fig. 1.

The isotherms show, first of all, that the content of oxygen in the solid phase is not a linear function of the partial pressure of atomic oxygen in the gaseous phase (or, which is the same thing, a linear function of the ratio P_{CO_2}/P_{CO}).

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* 1100-1350°.

** For example, according to the data of Jette and Foote [3] and Pfeil [5], at 1200° the oxygen-rich ferrous oxide contains 24.3% oxygen, while, according to the data of Darken and Garri, it contains 25.3%.

TABLE 1

Dependence of the composition of the solid phase on P_{CO_2}/P_{CO} in the gaseous phase in equilibrium with it

1104°K		1182°K	
Composition of the solid phase FeO (in mole %)	P_{CO_2}/P_{CO}	Composition of the solid phase FeO (in mole %)	P_{CO_2}/P_{CO}
1.008	0.53	0.95	0.47
1.032•	0.53	0.017•	0.47
1.047	0.58	1.042	0.51
1.057•	0.75	1.059•	0.79
1.075•	1.15	1.072•	1.05
1.089•	1.67	1.083	1.45
1.090	1.58	1.100•	2.12
1.092•	1.72	1.106•	2.51
1.096	1.95	1.107	2.85
1.097	2.01	1.116•	3.12
1.124	2.86	1.220	3.12
1.150•	2.86		

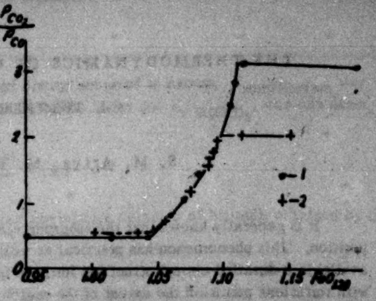

Fig. 1. Dependence of P_{CO_2}/P_{CO} on the composition of the solid phase. 1 – 1182°K; 2 – 1104°K.

Darken and Garri, having a significant dispersion of points, in view of the comparatively low precision of the experiments, constructed a straight line through them. Our data, which indicate the inapplicability of Henry's law in this case, appear to be considerably more natural.

That interval of composition of the solid phase in which the magnitude of the ratio P_{CO_2}/P_{CO} depends on the composition is taken by all authors as the region of homogeneity of ferrous oxide. Our data (Fig. 1) lead to a magnitude for the region of homogenity that is close to that found by other authors (Table 2).

TABLE 2

Author	Temp. (in °C)	Range in which ferrous oxide exists.
Darken and Garri [2] (extrapolation)	800	$FeO_{1.05}-FeO_{1.112}$
Jette and Foote [3]••	800	$FeO_{1.059}-FeO_{1.11}$
Matsubara [4]	863	$FeO_{1.055}-FeO_{1.127}$
Schenk [1]	800	$FeO_{1.04}-FeO_{1.13}$
Pfeil [5]	800	$FeO_{1.096}$
Our data	831	$FeO_{1.0425}-FeO_{1.0975}$
	909	$FeO_{1.0590}-FeO_{1.1075}$

The dependence of the equilibrium pressure of oxygen (O_2) on the composition of the solid phase is depicted in Figs. 2 and 3. The magnitudes of the equilibrium pressures of O_2 obtained from our data for the ratio P_{CO_2}/P_{CO} and the equilibrium constants for $CO_2 \rightleftarrows CO + \frac{1}{2}O_2$, were taken equal to $8.1 \cdot 10^{-17}$, for 1104°K and equal to $3.24 \cdot 10^{-16}$ [6] for 1182°K according to the formula:

$$P_{O_2} = K^2_{\text{equilibrium}} \left(\frac{P_{CO_2}}{P_{CO}}\right)^2.$$

If, from the course of the isotherm P_{CO_2}/P_{CO} – composition of the solid phase, a completely determined and clear-cut representation of the position of the lower boundary of the region of homogeneity of ferrous oxide is found, it is impossible to say this concerning the isotherms: P_{O_2} – composition of the solid phase.

The fact is that all the isotherms (Figs. 1, 2, 3) converge asymptotically toward the straight line portion corresponding to the region of heterogeneity; it is, therefore, difficult to establish the lower boundary of the region of homogeneity. This is particularly noticeable in utilizing the isotherm: P_{O_2} – composition, since its points are obtained by squaring the values of the ratio P_{CO_2}/P_{CO}.

Thus, the lower boundary of the region of homogeneity of ferrous oxide must be considered as not completely reliably established either by us or by the preceding authors.

The results of the roentgenographic investigations of Jette and Foote can not be considered conclusive here, inasmuch as these authors took the roentgenograms at room temperature, when ferrous oxide is in general metastable. The possibility is not excluded that the region of homogeneity of ferrous oxide extends down to the

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• These data refer to experiments in the course of which equilibrium was reached via reduction of the solid phase; the others – via oxidation.

•• The data of Jette and Foote were obtained in the course of X-ray investigations.

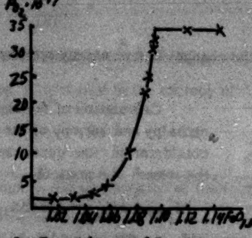

Fig. 2. Dependence of P_{O_2} (atm.) on the composition of the solid phase at 1104° K.

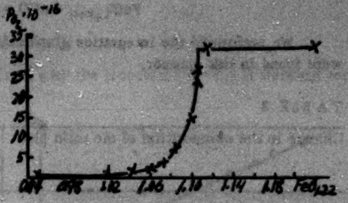

Fig. 3. Dependence of P_{O_2} (atm.) on the composition of the solid phase at 1182° K.

composition corresponding to the formula FeO. We propose to determine the lower boundary of the region of homogeneity, using phase analysis of determinations of magnetic susceptibility as the method.

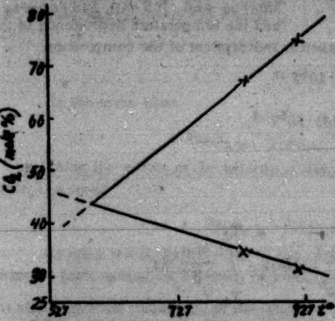

Fig. 4. Extrapolation of the equilibrium composition of the gas (corresponding to the upper and lower boundaries of the region of homogeneity of ferrous oxide) to the temperature at which this phase disappears.

The values found by us for the equilibrium composition of the gas (expressed in molecular percentages of CO_2), corresponding both to the upper and to the lower boundary of the region of homogeneity of ferrous oxide are shown in Figure 4.

Extrapolation of these data in an assumed linear dependence of P_{CO_2} on the temperature, leads to a temperature of disappearance of the wustite, equal to 591°C, which is close to the known value, found by experiment, of 572°C.

The Enthalpy of Formation and the Entropy of Ferrous Oxide of Various Compositions. At a temperature of 1104°K the lower boundary of the region in which ferrous oxide exists corresponds to a composition of $FeO_{1.0435}$, i.e., at 1104°K the phase with this composition is reduced to metallic iron as a result of reaction with the mixture CO_2/CO at a constant ratio (throughout the entire extent of the reduction process) of the partial pressures of these gases (we are here neglecting the portion corresponding to a solid solution of oxygen in iron—oxyferrite—since it can not introduce substantial error).

In conformity with this, the change in free energy corresponding to the process:

$$FeO_{1.0435} + 1.0435CO = Fe + 1.0435CO_2$$

at 1104°K, can be found by the generally-known formula:

$$\Delta F = -nRT \ln P_{CO_2}/P_{CO}.$$

At 1182°K the composition $FeO_{1.039}$ corresponds to the lower boundary of the region in which ferrous oxide exists, i.e., the change in free energy corresponding to the portion of the process:

$$FeO_{1.039} + 1.039CO = Fe + 1.039CO_2$$

can be found as in the preceding case.

As regards the portion of the process:

$$FeO_{1.0435} + 0.0045CO = FeO_{1.039} + 0.0045CO_2,$$

the change in free energy corresponding to it (at 1182°) can be found by the equation:

$$\Delta F = -RT \int_{x}^{x+n} \ln \frac{P_{CO_2}}{P_{CO}} \, dn,$$

since in this portion the process is completed at variable values of P_{CO_2}/P_{CO}. We were also obliged to find in similar fashion the values of the change in free energy corresponding to the other portions of the process:

$$FeO_{1+x+n} + nCO = FeO_{1+x} + nCO \qquad (a)$$

We performed the integration graphically. The magnitudes of the changes in free energy set down in Table 3 were found in this manner.

TABLE 3

Change in the composition of the solid phase	ΔF corresponding to the process (a) (in calories)	
	1104°K	1182°K
$FeO_{1.039} - FeO_{1.0425}$	—	+ 6.5
$FeO_{1.0425} - FeO_{1.05}$	+ 8.3	+ 9.0
$FeO_{1.05} - FeO_{1.06}$	+ 7.3	+ 8.0
$FeO_{1.06} - FeO_{1.07}$	+ 2.3	+ 2.5
$FeO_{1.07} - FeO_{1.08}$	− 2.9	− 3.1
$FeO_{1.08} - FeO_{1.09}$	− 8.0	− 8.6
$FeO_{1.09} - FeO_{1.0975}$	− 9.8	− 10.1

Calculation of the changes in enthalpy and entropy of the process under consideration was conducted by solving the system of equations

$$\Delta F_{1104} = \Delta H_{1104} - 1104\Delta S_{1104},$$

$$\Delta F_{1182} = \Delta H_{1104} + \Delta\Delta H - 1182(\Delta S_{1104} + \Delta\Delta S),$$

where quantities ΔΔH and ΔΔS– are auxiliary terms consisting of the changes, respectively, of ΔH and ΔS during the transition from 1140° to 1182°K. ΔΔH and ΔΔS were calculated on the basis of the values of the enthalpy of the conversion Feα→Feβ (165 cal), and Feβ→Feγ and the temperature dependence of the heat capacity of CO_2, CO, Fe, and ferrous oxide [6] (the latter was taken as independent of the composition.

$$CO_2: C_p = 10.34 + 2.74 \cdot 10^{-3}T - 1.955 \cdot 10^{5}T^{-2},$$
$$CO: C_p = 6.6 + 1.20 \cdot 10^{-3}T,$$
$$\text{"}FeO\ C_p = 12.62 + 1.492 \cdot 10^{-3}T - 0.762 \cdot 10^{5}T^{-2},$$
$$Fe_{\alpha}\ C_p = 4.13 + 6.38 \cdot 10^{-3}T,$$
$$Fe_{\beta}\ C_p = 11.50 + 12 \cdot 10^{-3}T,$$
$$Fe_{\gamma}\ C_p = 7 + 4 \cdot 10^{-3}T,$$

according to the formulas:

$$\Delta\Delta H = \Delta aT + \frac{\Delta b}{2}(T_2^2 - T_1^2) + \Delta C\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad \Delta\Delta S = \int_{T_1}^{T_2} \frac{\Delta C_p}{T}\, dT.$$

Thus, the values of the quantities $\Delta H_{1104°}$ and $\Delta S_{1104°}$ for all the processes set forth in Table 3 were found. The magnitudes of the changes in the enthalpy of the processes under consideration at 298°K were found by use of the same equations and the temperature dependence of the heat capacities of CO_2, CO, βFe, αFe, and FeO, and also of the magnitude of the enthalpy of the conversion of βFe into αFe (which occurs at 1050°K).

TABLE 4*

Composition of the solid phase	−ΔH of formation (in kcal.)	Composition of the solid phase	−ΔH of formation (in kcal.)
$FeO_{1.0425}$	65.973	$Fe_{0.9592}O$	63.231
$FeO_{1.05}$	66.439	$Fe_{0.9524}O$	63.2
$FeO_{1.06}$	67.159	$Fe_{0.9434}O$	63.360
$FeO_{1.07}$	67.877	$Fe_{0.9346}O$	63.447
$FeO_{1.08}$	68.594	$Fe_{0.9259}O$	63.510
$FeO_{1.09}$	69.310	$Fe_{0.9174}O$	63.585
$FeO_{1.0975}$	69.872	$Fe_{0.9112}O$	63.665

With the aid of these quantities and the values of the enthalpies of formation of CO_2 and CO (94.0 and 26.39 kcal respectively), the enthalpies of formation of ferrous oxides of various composition were calculated as set forth in Table 4. The dependence of the enthalpy of formation on the composition of the solid phase is presented graphically in Fig. 5. The entropy changes accompanying the process of gradual reduction of ferrous oxide by carbon monoxide are summarized in Table 5.

At 298°K the change in the entropy of the processes (3) – (6) should be less than that at 1104°K by 0.061 cal/1° (we found this quantity as

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* We express the composition of ferrous oxide both as $Fe_{1-x}O$ and as FeO_{1+x}. The first method of transcription seems more correct from the point of view of the structure of this compound, but the second method is more widely employed.

$$\int_{298}^{1104} \frac{\Delta C_p}{T}\, dT,$$

assuming the heat capacity of $FeO_{1.06}$, $FeO_{1.05}$ and so forth, to be identical).

Thus, a reduction in the entropy of 0.06-0.05 cal./1° is associated with the processes (3) −(6) at standard temperature.

TABLE 5

Process	Change in the composition of the solid phase	ΔS in cal/1° (at 1104°)
1	$FeO_{1.0435} + 1.0435\ CO = Fe + 1.0435\ CO_2$	−4.924
2	$FeO_{1.05} + 0.0065\ CO = FeO_{1.0435} + 0.0065\ CO_2$	−0.0083
3	$FeO_{1.06} + 0.01\ CO = FeO_{1.05} + 0.01\ CO_2$	−0.011
4	$FeO_{1.07} + 0.01\ CO = FeO_{1.06} + 0.01\ CO_2$	−0.004
5	$FeO_{1.08} + 0.01\ CO = FeO_{1.07} + 0.01\ CO_2$	+ 0.0013
6	$FeO_{1.09} + 0.01\ CO = FeO_{1.08} + 0.01\ CO_2$	+ 0.006
7	$FeO_{1.0975} + 0.0075\ CO = FeO_{1.09} + 0.0075\ CO_2$	+ 0.0034

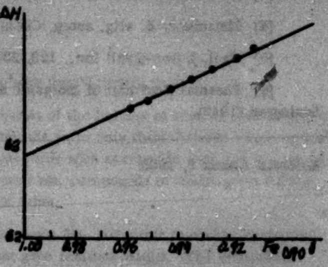

Fig. 5. D ependence of $\Delta H_{formation}$ (in kcal) on the composition of ferrous oxide.

At the same time

$$S_{FeO_{1.06}} - S_{FeO_{1.05}} = 0.01\,(S_{CO_2} - S_{CO}) + 0.06.$$

Using the values of the entropy at 298°K for CO_2 (51.08 cal./mole/1°) and CO (47.32 cal./mole/1°), we obtain as a result

$$S_{FeO_{1.06}} - S_{FeO_{1.05}} = 0.1\ \text{cal./mole/1°}.$$

In other words, the increase in the content of oxygen in ferrous oxide is accompanied byan increase in the entropy (calculating on 1 g-atom of iron). Even in calculating on 1 g-atom (both of iron and of oxygen) the entropy is also somewhat increased $\left(\text{by the quantity } \frac{S_{FeO_{1+x}}}{2+x}\right)$.

However, it is evident from Table 5 that this increase in entropy is somewhat retarded in proportion to the increase in oxygen content in the ferrous oxide. This appears to be the cause of the fact that the graph of the pressure of O_2 against the composition of the solid phase changes curvature and becomes more and more steep, which determines the break in the region of homogeneity of ferrous oxide on the side bordering on Fe_3O_4.

SUMMARY

1. The equilibrium of the process of the reduction of ferrous oxide by mixtures of CO_2/CO at temperatures of 1104 and 1182°K was investigated.

2. In the investigated temperature range, the equilibrium constant of the process $FeO_{1+x+y} + yCO \rightleftarrows FeO_{1+x} + yCO_2$ within the limits of the region of homogeneity of ferrous oxide, is practically independent of the temperature.

3. The upper limit of the region of homogeneity of ferrous oxide corresponds to a composition of $FeO_{1.0975}$ at 1104°K and of $FeO_{1.1075}$ at 1182°K.

4. It was established that the dependence of the equilibrium pressure of atomic oxygen on the composition of the solid phase did not obey Henry's law.

5. It was established that the entropy of ferrous oxide, calculated for 1 g-atom, is somewhat increased in proportion to the increase in the content of oxygen in this phase.

6. The magnitudes of the enthalpies of formation of ferrous oxide of various compositions at standard conditions (Table 4) were found. The magnitude of the enthalpy of formation of ferrous oxide appears to be a linear function of its composition.

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PHYSICO-CHEMICAL ANALYSIS OF THE SYSTEM:

ALUMINUM CHLORIDE – ACETAMIDE – WATER

B. Ya. Rabinovich

Acetamide as an addendum in complex formation reactions has been insufficiently studied.

B. N. Menshutkin [1, 2, 4], while investigating molecular compounds of the halides of several metals of the first and second main subgroups, established that compounds with acetamide form only those halides which crystallize from aqueous solutions in the form of hydrates; the molecular compounds with acetamide with any degree of strength yield almost no hydrates. According to the data of B. N. Menshutkin, compounds of magnesium halides with acetamide are stronger than compounds with alcohol, acetone and ether.

$NaBr \cdot 2CH_3CONH_2$ and $NaI \cdot 2CH_3CONH_2$ are described in the literature [2]. Attempts to obtain analogous compounds of sodium chloride and also of the potassium halides did not give positive results. The compound $KI \cdot 6CH_3CONH_2$ obtained by Walker and Jahnson [3] with a melting point of 59°, as was shown by B. N. Menshutkin [1], does not exist. Walker and Jahnson mistook a eutectic with the same melting point and composition for a compound.

On the other hand, there is a great analogy in the physico-chemical properties of water and acetamide. Acetamide, like water, possesses high dielectric properties. The dielectric constant of acetamide is 59.1 [5]. Mineral salts are quite soluble in fused acetamide and form solutions with acetamide which readily conduct an electric current. The investigations of Walker and Jahnson [3] of the electrical conductivity of solutions of certain mineral salts in acetamide demonstrated that the molecular conductivity was approximately identical for aqueous and acetamide solutions.

The cryoscopic investigations of acetamide solutions of mineral salts conducted by Bruni and Manuelli [6], showed that the salts are almost completely dissociated.

Aluminum chloride forms a hydrate with six molecules of water: $[Al(H_2O)_6]Cl_3$. Attempts to obtain a complex compound of aluminum chloride with acetamide by crystallization of aqueous, water-alcohol and hydrochloric acid solutions were not crowned with success.

The results of an investigation of complex formation of aluminum chloride with acetamide by the methods of physico-chemical analysis are presented in the present article.

EXPERIMENTAL

We determined the specific gravity, viscosity and electrical conductivity at 18, 25 and 35°, and also conducted cryoscopic investigations of the system: aluminum chloride – acetamide – water.

We used chemically pure aluminum chloride hexahydrate for the work. 43.63% chlorine was found in the preparation. The result obtained by calculation from the formula: $AlCl_3 \cdot 6H_2O$ is 44.07%. Acetamide was recrystallized from alcohol and dried at 50-60°. The melting point of the preparation obtained was 81°. The viscosity was determined with an Ostwald viscosimeter.

The solutions for the investigation were prepared by the method of isomolar concentrations proposed by Ostromyslensky [7]. 0.25 molar solutions of aluminum chloride and acetamide were mixed in various volume ratios at constant total volume.

The results of the measurements of specific gravity, viscosity and specific electrical conductivity are presented in Tables 1, 2, 3 and in Figs. 1 and 2.

The temperature coefficients of viscosity and electrical conductivity which are presented in Table 4 and Fig. 2 (curves 4 and IV) were calculated from the data obtained.

TABLE 1

The system: $AlCl_3-CH_3CONH_2-H_2O$
Temperature 18°

Molar percent of acetamide	d_4^{18}	Viscosity (in centipoises). $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0269	1290.5	42.5
33.3	1.0186	1226.1	30.6
50	1.0135	1189.2	23.9
66.7	1.0094	1160.0	17.1
75	1.0072	1146.8	13.3
80	1.0049	1132.0	11.0
85.7	1.0035	1122.0	8.2
91.7	—	—	5.3
100	1.0001	1098.6	0.22

TABLE 2

The system: $AlCl_3-CH_3CONH_2-H_2O$
Temperature 25°

Molar percent of acetamide	d_4^{25}	Viscosity (in centipoises). $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0254	1084.9	48.9
33.3	1.0161	1028.1	34.9
50	1.0119	998.6	27.4
66.7	1.0072	975.1	19.8
75	1.0053	960.5	15.4
80	1.0034	948.8	12.6
85.7	1.0020	939.9	9.8
91.7	—	—	6.0
100	0.9980	919.0	0.25

TABLE 3

The system: $AlCl_3-CH_3CONH_2-H_2O$
Temperature 35°

Molar percent of acetamide	d_4^{35}	Viscosity (in centipoises). $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0226	879.5	58.0
33.3	1.0134	837.0	41.6
50	1.0088	817.4	31.6
66.7	1.0040	795.4	23.8
75	1.0021	780.3	18.6
80	1.0002	775.0	15.3
85.7	0.9989	768.0	11.5
91.7	—	—	7.3
100	0.9951	749.3	0.30

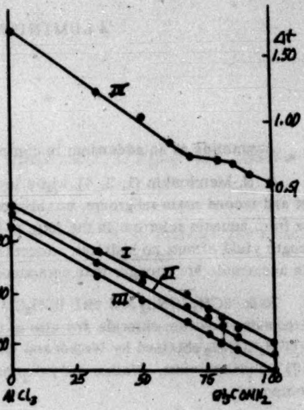

Fig. 1. The system: $AlCl_3-CH_3CONH_2-H_2O$. Specific gravity: I – 18°; II – 25°; III – 35°; IV – temperature depression.

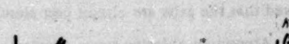

Fig. 2. The system: $AlCl_3-CH_3CONH_2-H_2O$. Specific electrical conductivity: I – 18°; II – 25°; III – 35°; IV – temperature coefficient of electrical conductivity. Viscosity: 1 – 18°; 2 – 25°; 3 – 35°; 4 – temperature coefficient of viscosity.

Cryoscopic investigations of the system were conducted in a Beckmann apparatus. Solutions containing considerable quantities of acetamide crystallized with difficulty. To avoid considerable supercooling, we were compelled to elicit crystallization by the addition of a primer – small ice crystals. The results of the measurements of the temperature depression of the system are shown in Table 5 and Fig. 1, Curve IV.

TABLE 4

The system: $AlCl_3-CH_3CONH_2-H_2O$
Temperature coefficients of viscosity and electrical conductivity

Molar percent of acetamide	Temperature coefficient	
	Viscosity	Electrical conductivity
0	–0.0187	0.0186
33.3	–0.0183	0.0192
50	–0.0184	0.0153
66.7	–0.0185	0.0202
75	–0.0188	0.0208
80	–0.0186	0.0214
85.7	–0.0186	0.0173
91.7	–	0.0217
100	–0.0187	0.0200

TABLE 5

Cryoscopy of the system: $AlCl_3-CH_3CONH_2-H_2O$

Molar percent of acetamide	Temperature depression Δt (in degrees)
0	1.72
33.3	1.23
50	1.04
66.7	0.85
75	0.74
80	0.71
85.7	0.68
91.7	0.61
100	0.52

The temperature depression of a 0.25 molar solution of aluminum chloride amounted to 1.72° according to our data. The apparent degree of dissociation of aluminum chloride calculated according to the formula $\alpha = \frac{\Delta t' - \Delta t}{\Delta t(m-1)}$ was equal to 0.88. The lowering of the freezing point of a 0.25 molar acetamide solution amounted to 0.52°. The molecular weight of acetamide calculated according to these data was 53.5, according to the formula CH_3CONH_2 – 59. The reduction in the molecular weight of acetamide was probably associated with partial hydrolysis of acetamide proceeding according to the scheme:

$$CH_3CONH_2 + 2H_2O \rightleftharpoons CH_3COOH + NH_4OH.$$

The degree of hydrolysis can be calculated by the same formula, taking $\underline{m} = 2$. The degree of hydrolysis calculated in that way is equal to 0.13.

Discussion of Results

As is evident from Figs. 1 and 2, the specific gravity and viscosity of the system was found to be a linear function of the concentration of acetamide. The temperature coefficient of viscosity (Fig. 2) has the same value for all compositions of the system.

The isotherms of specific gravity and viscosity did not give any indications of chemical reaction of the components of the system. The isotherms of specific electrical conductivity (Fig. 2) deviate from rectilinearity, giving some deflection at 50% acetamide and a particularly sharp deflection at 85.7% acetamide which corresponds to a molar ratio of aluminum chloride to acetamide of 1:6.

The temperature coefficient of electrical conductivity (Fig. 2) forms two minimums at the very points corresponding to compositions of 1:1 and 1:6.

The temperature depression of the system (Fig. 1) is diminished irregularly in proportion to the increase in the concentration of acetamide. As a consequence of the dissociation of aluminum chloride, which proceeded to a greater extent than the hydrolysis of acetamide, the concentration of particles in the solution did not remain constant, but diminished in proportion to the increase in acetamide, at the beginning very sharply, and then was retarded, which was reflected in the course of the curve of the dependence of the temperature depression on the composition of the system. However, in the region of acetamide concentration of 85.7% (molar ratio 1:6) there is some slope of a section after which a rectilinear diminishing of the depression sets in, which, probably, is associated with a weak chemical reaction in the system.

Thus, only the isotherms of electrical conductivity and cryoscopic measurements give any indication of a chemical process proceeding in the system.

According to Kurnakov [8], viscosimetry is a more sensitive method of physico-chemical analysis than electrical conductivity measurements. However, the isotherms of viscosity of the given system do not have any singular points, in contrast to the electrical conductivity isotherms. But this character of linear dependence of the viscosity of a mixture of two solutions on the composition is itself, to a certain extent, anomalous. The viscosity of an ideal mixture is not linearly dependent on the composition [9], but has a hyperbolic character. The linear dependence of the viscosity in our system can be explained by analogy with the physico-chemical properties of water and acetamide. Among the other factors determining the viscosity of a substance, the intermolecular forces have an essential significance. As a consequence of the great similarity in the physico-chemical properties of water and acetamide, substitution of water molecules for acetamide molecules does not substantially change the molecular reactive forces, and, therefore, is not reflected in the viscosity of the system.

It is usually considered that metallic ions with the electron shell of an inert gas form complex compounds primarily at the expense of electrostatic forces [10]; at the same time, an important role is played, on the one hand, by the charge of the metallic ion and its radius, and on the other hand, by the magnitude of the permanent dipole of the addendum. The polarization forces play a secondary role [11]. The permanent dipole moment of acetamide, according to the data of Bates and Hobbs [12], is equal to 3.44 D, i.e., approximately 2 times greater than the dipole moment of water. Nevertheless, acetamide does not form stable complex compounds with aluminum halides in aqueous solution. The formation of molecular compounds as a result of an ion dipole reaction is characteristic of the alkaline and the alkaline earth metals. Aluminum, possessing a high ionization potential and a small electron affinity, primarily forms covalent bonds. In aqueous solution the hydrated ion of aluminum preserves the octahedral structure characteristic of the crystallohydrate $[Al(H_2O)_6]Cl_3$ [13], in which 6 molecules of water are bound covalently to the aluminum ion. The aluminum ion can be hydrated by a large number of water molecules, but the part of the water molecule forming the last shell is bound with the ion $[Al(H_2O)_6]^{\cdot\cdot\cdot}$ by electrostatic bonds. Starting with these concepts, we can assume that stable water-soluble compounds can be formed only with addenda having the capacity to form a more covalent bond with the aluminum ion than the $Al-OH_2^{*}$ bond, or if the bond is strengthened by ring formation.

Acetamide, although it contains trivalent nitrogen, can not form a more covalent bond, since the donor property of nitrogen is greatly weakened by the presence of the carbonyl group. As was shown by Chernyaev and Nazarova [14], acetamide does not form the usual type of complex compound with divalent platinum salts. The substance obtained by them of the composition $Pt(NHCOCH_3)_2 \cdot H_2O$ (diacetimideplatinum) is, according to its character, an internal-complex compound. In this compound platinum forms a valent bond with nitrogen at the expense of the hydrogen of the amide group.

Aluminum forms internal-complex compounds stable in aqueous solution primarily with organic substances possessing acidic properties. The acidic function of acetamide is very weakly expressed. The dissociation constant of acetamide as an acid is equal to $8 \cdot 10^{-16}$ [15]. Taking into account the weakly basic property of aluminum hydroxide, the possibility of formation of internal-complex compounds of the aluminum ion with acetamide at the expense of the valent bond with the nitrogen of the amide group is improbable. This causes the instability of acetamide complexes of aluminum halides in aqueous solution.

SUMMARY

1. The specific gravity, viscosity and electrical conductivity of the system: aluminum chloride – acetamide – water at 18, 25 and 35° was measured by the method of isomolar concentrations.

2. The specific gravity and viscosity were found to be linearly dependent on the composition of the system. The isotherms of the specific electrical conductivity had a bend at a molar ratio $AlCl_3 : CH_3CONH_2$, equal to 1:1 and 1:6.

3. The temperature coefficient of viscosity has a constant value and does not depend on the concentration of acetamide in the system. The temperature coefficient of specific electrical conductivity has two minima, which correspond to molar ratios of 1:1 and 1:6.

4. The temperature depression of the system diminishes with increase in the concentration of acetamide. In the region of acetamide concentration corresponding to a molar ratio $AlCl_3 : CH_3CONH_2$ = 1:6, the fall in the depression is retarded and the curve Δt – composition in this region has a rather inclined section.

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[*] The instability in aqueous solution of aluminum ammoniates is evidently exclusively associated with the low solubility of aluminum hydroxide.

5. The apparent degree of dissociation of aluminum chloride as a tetraionic electrolyte calculated from cyroscopic data amounts to 0.88. The molecular weight of acetamide in 0.25 molar solution was found to be equal to 53.5.

6. The instability of the acetamide complex of aluminum chloride in aqueous solution was explained by weakening of the donor properties of the nitrogen of the amide group, by the presence of the carbonyl group and the impossibility of formation of compounds of the internal-complex type, in view of the weakness of the acidic properties of acetamide.

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PHYSICO-CHEMICAL INVESTIGATION OF THE REACTION OF TITANIUM TETRACHLORIDE WITH ETHYL ACETATE

Yu. A. Lysenko and O. A. Osipov

In the preceding articles [1, 2] we have shown that in systems composed of titanium tetrachloride and esters of monobasic acids, rather stable molecular compounds are formed in the liquid phase; at the same time, a complex of the composition $TiCl_4 \cdot E$ (where E = a molecule of ester) is more characteristic of titanium tetrachloride, in contrast to stannic tetrachloride which reacts with two molecules of ester. We attempted to explain this fact on the basis of the difference in the magnitudes of the tetrahedral covalent radii of titanium and tin. Investigation of a number of properties (viscosity, density, electrical conductivity) of the system was undertaken with the goal of obtaining further experimental basis for the earlier expressed hypothesis.

EXPERIMENTAL AND DISCUSSION OF RESULTS

We used c.p. titanium tetrachloride and ethyl acetate for the investigation. The latter was dried for a long time over calcium chloride after which it was twice redistilled. The fraction with a b.p. 77.1-77.8°; $d_D^{19.2}$ 0.8998; $n_D^{19.2}$ 1.3722 was used.

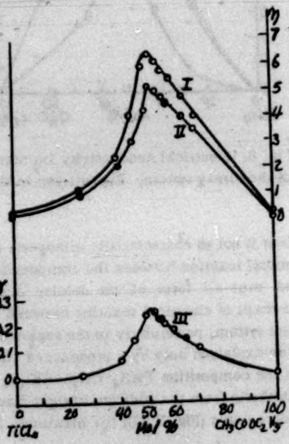

Fig. 1. Isotherms of viscosity. I – 97°; II – 102°; III – absolute temperature coefficient of viscosity.

The methods for preparing the solutions and measuring the density, viscosity and electrical conductivity have been described previously [1]. The system was investigated at temperatures of 97 and 102°. The outer temperature limits were determined on the one hand by the rapid formation of crystals below 97°; on the other hand, by the circumstance that at temperatures above 102-105° change in the color of the melt from light yellow to brown began, which evidently is associated with partial resinification. The change in color was the more intense, the richer the melt in titanium tetrachloride.

In Fig. 1 (I and II) the results of the measurements of viscosity, expressed in centiposes for the two temperatures * are presented.

The viscosity isotherms, as is evident, pass through a pronounced maximum corresponding to 53 mole % of ethylacetate,, i.e., it is somewaht deflected to the side from the unit ratio of the components of 1:1. On the basis of the form of the viscosity isotherm one can definitely conclude that in the system: titanium tetrachloride – ethyl acetate, a molecular compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$ is formed in the liquid phase.

The pronounced maxima on the viscosity isotherms at 97 and 102° indicate the considerable thermal stability of the complex obtained. At 97° the viscosity maximum is 17.4 times greater than the viscosity of the most viscous component, and at 102° it is 14.8 times greater. It should be noted that, while the branch of the viscosity isotherm adjacent to the titanium tetrachloride is convex toward the composition axis for its entire extent, the branch adjacent to the ester is a straight line (and even somewhat convex toward the composition axis at 102°). This fact is evidence of the absence of chemical reaction between titanium tetrachloride and the molecular compound obtained.

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* The data for 100% $CH_3COOC_2H_5$ are taken from [4].

The results of the calculation of the absolute temperature coefficient of viscosity are set forth in Fig. 1, III. The curve of the temperature coefficient as a function of the composition passes through a maximum corresponding to an almost equimolecular ratio of the components, and consequently, also confirms the existence of the compound $TiCl_4 \cdot CH_3COOC_2H_5$.

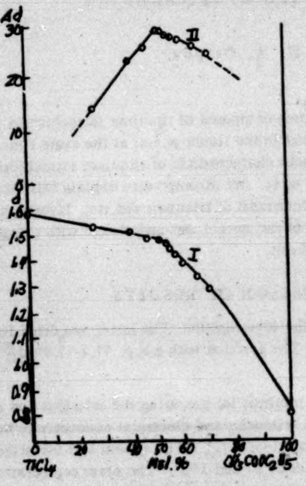

Fig. 2. Density isotherms of the binary system. Explanation in the text.

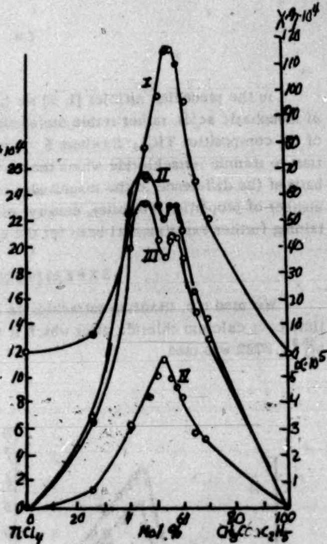

Fig. 3. Electrical conductivity isotherms of the binary system. Explanation in the text.

The results of the measurements of density at 102° are presented in Fig. 2, I. Here we do not cite an isotherm at 97° since it almost coincides with the isotherm at 102°, due to the low temperature coefficient.

Numerous experimental data indicate that the density of the system is not so characteristic a property as, for example, the viscosity, which serves to establish the presence of a chemical reaction between the components and to determine the composition of the compound obtained. However, the over-all form of the density diagram will indicate the condensation in the system which can be a result of chemical reaction between the components. As is evident from Fig. 2, significant condensation occurs in our system, particularly in the region of 45-55 mole % of ethyl acetate. Such a great condensation of the system can be explained only by a pronounced chemical reaction between the components, with the formation of a compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$. If we plot the numerical value of the deviation of the experimental density isotherm from the additive straight line along the ordinate axis, and the composition along the abscissa, then we obtain a curve (Fig. 2, II), the maximum of which corresponds to the composition of the compound.

The data of the measurements of electrical conductivity of the system are presented in Fig. 3.

The conductivity isotherms consist of curves having two maxima and one pronounced minimum corresponding to 53 mole % of ethyl acetate (Fig. 3, II and III).

According to the character of the conductivity curves, our system is formed from nonconducting components which, chemically reacting, yield a compound that can conduct a current [3].

In Fig. 3 (I and IV) are also set forth the curves of the absolute temperature coefficient and the reduced electrical conductivity. Both curves pass through sharp maxima, corresponding to the composition of the compound.

SUMMARY

1. The viscosity, density and electrical conductivity of the system: titanium tetrachloride—ethyl acetate, at temperatures of 97 and 102° were measured.

2. It was shown that titanium tetrachloride forms a molecular compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$ with ethyl acetate, in contrast to stannic tetrachloride, which reacts with two molecules of the ester.

3. It was shown that the results of our investigations of the composition ratio of the obtained compound confirm the earlier expressed hypothesis.

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• See Consultants Bureau Translation, page 1177.

SUMMARY

1. The [illegible] density, and [illegible] of [illegible] were measured.

2. It was shown that [illegible] forms a [illegible] compound [illegible] with [illegible].

3. It [illegible] that the results of our [illegible] in the [illegible] the [illegible] hypothesis.

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KINETICS OF THE AQUATIZATION OF UREA COMPLEXES OF CHROMIUM

K. B. Yatsimirsky and E. I. Yasinskene

One of the peculiarities of complex compounds of trivalent chromium is that they are formed and decomposed rather slowly in aqueous solutions. In contrast to the other elements of the fourth period of the Mendeleev periodic table, which form complexes(along with slowly reacting complexes), that are decomposed instantly, all the complex compounds of chromium which have been studied are decomposed with measureable speed [1].

The exchange kinetics of complexly bound water in ions of the type $M(H_2O)_6^{3+}$ (M=Al, Fe, Co, Ga, Cr) was recently studied by the method of labeled atoms; it was shown that only in the case of the hexahydrate of the chromium ion does the water exchange process proceed with measureable speed [1]; in all the other cases the equilibrium state was reached instantly.

The rather high stability of the very numerous complex compounds of chromium in aqueous solutions is evidently to be explained by the slowness of aquatization (substitution of water molecules in the internal spheres of the addenda). The circumstance that the overwhelming majority of the complexes of trivalent chromium can not be obtained by the direct route in aqueous solution argues in favor of this hypothesis.

The preparative aspects of the complex hexaurea chromium salt havebeen studied rather thoroughly [3, 4]. These salts can not be obtained via simple mixture of the constituent parts in aqueous solution. If these salts are obtained by evaporating the solution to dryness, then the ion $[Cr(CON_2H_4)_6]^{3+}$ can be detected in the solution for a rather prolonged time.

The first attempt to study the kinetics of the aquatization of hexaurea chromium salts was made by Kilpatrik [4]. This author studied the rate of the reaction at only one temperature (22.5°), and arbitrarily assumed the complete substitution of urea molecules by water according to the scheme:

$$[Cr(CON_2H_4)_6]^{3+} + 6H_2O = [Cr(H_2O)_6]^{3+} + 6CON_2H_4.$$

To enumerate the activation energy and the preexponential factor it was necessary to study the rate of this reaction at several temperatures. The assumption concerning complete displacement of urea molecules from the inner sphere appeared baseless to us and required additional testing.

EXPERIMENTAL

As starting substance hexaurea chromic chloride $[Cr(CON_2H_4)_6]Cl_3$, was synthesized and purified by the method of Pfeiffer [5]. The purity of the preparation obtained was controlled by analysis for chromium content.

TABLE 1

Rate Constants of the Aquatization Reaction of the Hexaurea Chromic Ion at 30°

Time (in minutes	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4(in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})
0	23.95	–	47.13	–	70.82	–
720	18.09	3.90	36.43	3.58	54.52	3.63
1440	13.50	3.98	27.36	3.78	41.27	3.75
2160	10.09	4.00	19.87	4.00	30.06	3.88
2880	8.31	3.68	15.54	3.85	23.18	3.88
3600	6.62	3.57	11.87	3.83	17.07	3.95
4320	4.33	3.96	8.41	3.99	12.74	3.97
Mean value	–	3.85	–	3.84	–	3.84

Mean value $K = 3.84 \cdot 10^{-4}$ minutes^{-1}.

TABLE 2

Rate constants of the aquatization reaction of the hexaurea chromic ion at 40°

Time (in minutes)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)
0	47.14	–	45.40	–
120	38.46	17.0	–	–
240	33.00	14.9	30.76	16.2
360	26.05	16.5	–	–
480	22.33	15.6	21.09	16.0
600	18.36	15.7	–	–
720	13.13	15.8	14.64	15.7
840	–	–	10.67	17.2
960	–	–	8.44	17.5
Mean value	–	15.9	–	16.5

Mean value K 1.62 · 10^{-3} minutes $^{-1}$.

In contrast to the method used by Kilpatrik [4], the content of $[Cr(CON_2H_4)_6]^{3+}$ in the solution was determined by a volumetric method proposed by us. The essence of this method consisted of adding to the solution under investigation an excess of a titrated solution of $K_4Fe(CN)_6$. The complex ion then precipitated quantitatively in the form of the salt $[Cr(CON_2H_4)_6]_4[Fe(CN)_6]_3$; the product of the aquatization of the ferocyanide salt did not precipitate. The excess ferrocyanide was determined by titration with permanganate.

A determined weighed portion of hexaurea chromic chloride was dissolved in water and the solution obtained was stirred in an ultrathermostat in which constant temperature was maintained with a variation of ± 0.05°. After a determined interval of time, samples of the solution were removed and the hexaurea chromic ions were at once precipitated with excess titrated solution of potassium ferrocyanide. After 30 minutes the precipitate was filtered through a dry filter and a determined volume of the filtrate was titrated with permanganate solution. On the basis of these data the

TABLE 3

Rate constants of the aquatization reaction of the hexaurea chromic ion at 50°

Time (in minutes)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)
0	22.38	–	47.07	–	71.12	–	95.85	–
120	9.37	72.5	19.26	74.5	–	–	36.80	79.7
180	6.18	71.5	13.69	68.7	18.96	74.0	27.39	69.6
240	4.48	67.0	9.67	66.0	12.77	72.0	17.12	71.8
300	2.98	67.2	6.59	65.5	8.15	72.5	13.69	64.8
360	1.49	75.2	4.28	67.2	5.70	70.4	8.56	67.1
Mean value	–	70.7	–	68.4	–	72.2	–	70.7

Mean value K 7.06 · 10^{-3} minutes $^{-1}$.

TABLE 4

Rate constants of the aquatization reaction of the hexaurea chromic ion at 60°

Time (in minutes	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes $^{-1}$)
0	23.05	–	46.72	–	69.45	–
30	11.05	24.5	21.47	25.9	34.10	23.7
60	5.37	24.3	11.68	23.1	15.47	25.0
90	2.53	24.6	6.00	22.8	7.89	24.2
120	1.26	24.2	1.89	25.7	3.16	25.8
Mean value	–	24.4	–	24.4	–	23.7

Mean value K 2.45 · 10^{-3} minutes $^{-1}$.

concentration of the hexaurea chromic ions in the solution was calculated. A summary of the results obtained is set forth in Tables 1, 2, 3 and 4.

The rate constants were enumerated in all cases from the equation for monomolecular reactions. The values obtained for the rate constants are summarized in the same tables.

The optical characteristics of the solutions under investigation were subsequently studied on a universal photometer FM-2. The absorption spectrum of a freshly-prepared solution of hexaurea chromic chloride is set forth in Fig. 1.

In the course of time, the absorption spectrum of the solution changes in dependence on the temperature and with greater or less speed approaches to a fixed limit. The absorption spectrum of a solution containing the products of the aquatization of hexaurea chromic chloride, which does not change with time, is summarized in the same Fig. 1. This absorption spectrum is different from the absorption spectrum of aqueous solutions of chromic chloride.

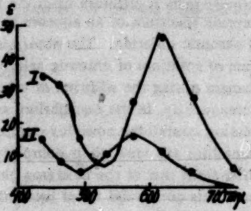

Fig. 1. Absorption spectra of aqueous solutions of hexaurea chromic salts (I) and the products of aquatization (II). Explanation in the text.

The data presented show that during the decomposition of hexaurea chromic chloride the optical density changes most strongly in the wave length intervals 600-680 and 440-480 mμ. This circumstance was utilized by us in the study of the rate of aquatization of hexaurea chromic salts in aqueous solution.

Samples were taken from the solutions of hexaurea chromic salts mixed in the ultrathermostat after a fixed interval of time and poured into ice water. The samples removed together with the added ice water were reduced to determined volume and the optical density of the solutions was measured on a FM-2 photometer with filters with an effective wave length of 465, 619 and 665 mμ. The measurements were conducted at two temperatures (40 and 50°), and the initial concentration of the solutions was 0.04 and 0.05 molar. The results obtained are summarized in Tables 5 and 6.

TABLE 5

Rate constants of the aquatization reaction of the hexaurea chromic ion found by the optical method at 40° (Initial concentration of hexaurea chromic salt 0.05 molar)

Time (in minutes)	Light filter with λ = 665 mμ			Light filter with λ = 619 mμ			Light filter with λ = 465 mμ		
	D	$1-a$	10^3 K	D	$1-a$	10^3 K	D	$1-a$	10^3 K
0	1.32	1.000	–	2.32	1.000	–	1.57	1.000	–
120	1.19	0.881	1.06	2.15	0.901	0.87	1.43	0.880	1.08
240	1.10	0.798	0.94	1.96	0.791	0.98	1.32	0.786	1.00
360	0.99	0.697	1.00	1.76	0.675	1.09	1.20	0.684	1.05
480	0.90	0.615	1.01	1.62	0.594	1.08	1.10	0.598	1.07
600	0.82	0.541	1.03	1.50	0.523	1.08	1.03	0.538	1.04
720	0.77	0.495	0.98	1.40	0.471	1.05	0.99	0.496	0.96
∞	0.23	0.000	–	0.60	0.000	–	0.40	0.000	–

Mean value K $1.02 \cdot 10^{-3}$ minutes^{-1}.

Note. In Tables 5 and 6, D denotes the optical density, $1-a$ denotes the portion of unreacted salt, and K denotes the rate constant.

If we denote by D_1, D_2 and D respectively the initial, final and intermediate optical density and by $1-a$ the portion of the salt remaining unchanged, then we obtain the following relationship:

$$D = D_1(1-a) + D_2 a. \qquad (1)$$

From this the amount of salt remaining at any moment can be calculated according to the equation:

$$1-a = \frac{D-D_2}{D_1-D_2}; \qquad (2)$$

and the rate constant from the equation for monomolecular reactions:

$$K = \frac{2.303}{t} \log (1 - a). \qquad (3)$$

The values of the rate constants enumerated in this manner, are summarized in the same Tables 5 and 6.

TABLE 6

Rate constants of the aquatization reaction of the hexaurea chromic ion, found by the optical method at 50° (Initial concentration of hexaurea chromic salt 0.041 molar)

Time (in minutes)	Light filter with λ = 665 mμ D	1− a	10^3 K	Light filter with λ = 465 mμ D	1−a	10^3 K
0	1.10	1.000	–	1.30	1.000	–
120	0.73	0.594	4.33	0.89	0.577	4.60
180	0.58	0.429	4.71	0.75	0.433	4.65
240	0.48	0.319	4.75	0.64	0.320	4.73
300	0.40	0.231	4.88	0.55	0.227	4.94
	0.190	0.000	–	0.33	0.000	–
Mean value	–	–	4.67	–	–	4.73

Mean value K $4.70 \cdot 10^{-3}$ minutes^{-1}.

It was indicated above that the absorption spectrum of a solution containing the end products of the aquatization of chromic salts is different from the absorption spectrum of an aqueous solution of chromic chloride. The absorption spectrum of solutions of chromic salts slowly changes during the addition of urea to them. Consequently, in the equilibrium state in a solution containing complex compounds of chromium and urea, their composition will differ from that of the hexaurea chromic ion. This compound is not precipitated by ferrocyanide and is different in its absorption spectrum from hexaurea chromic salts.

In order to establish the composition of the compound being formed at the attainment of equilibrium, we utilized the method of Ostromyslensky-Zhob. Solutions of chromic chloride and urea of identical molarity (0.038 and 0.38 molar) were mixed in various ratios; after the passage of three days the optical density of the solutions was measured with light filters with effective wave lengths of 436 and 465 mμ. Preliminary experiments established that the optical density of the solutions under investigation reached fixed values and did not substantially change further. The results of the experiments are summarized in Table 7.

TABLE 7

Optical density of solutions containing $CrCl_3$ and urea

Ratio of the number of moles of $CrCl_3$ to CON_2H_4	Optical density Found	Calculated	Discrepancy in the values for the optical density
1:9	0.31	0.29	0.02
2:8	0.61	0.58	0.03
3:7	0.85	0.87	−0.02
4:6	1.11	1.16	−0.05
5:5	1.35	1.45	−0.10
6:4	1.55	1.74	−0.19
7:3	1.95	2.03	−0.08
8:2	2.24	2.32	−0.08
9:1	2.48	2.61	−0.13

The optical density in the assumed absence of reaction between the chromic salts and urea was calculated for all the solutions investigated and the magnitudes of the discrepancies of the measured optical density from that theoretically calculated were found. The values of the discrepancies are summarized in the same Table 7; the maximum discrepancy in both cases was observed between ratios of the number of moles of Cr : CON_2H_4 1:1 and 1.5:1. Evidently a compound of the type $[Cr(CON_2H_4)(H_2O)_5]^{3+}$ is formed at the moment of achieving equilibrium in the system.

DISCUSSION OF RESULTS

The data set forth in Tables 1-6 are evidence of the fact that the values of the rate constant calculated in the assumed applicability to the aquatization reaction of hexaurea chromic ion of the equation for first order reactions, maintain a very satisfactory constancy.

The difference in the values of the rate constant calculated on the basis of the study of the optical density measurements at the time of, and according to the results of titration is worthy of attention. The constants obtained from the optical data remain approximately constant, but they are approximately 1.6 times less in absolute value than those found as a result of the chemical analysis of the solution.

This sort of decomposition can be explained if we assume that the aquatization process of the hexaurea chromic salts occurs in several stages:

$$\text{I} - [Cr(CON_2H_4)_6]^{3+} + H_2O = [Cr(CON_2H_4)_5 \cdot H_2O]^{3+} + CON_2H_4,$$

$$\text{II} - [Cr(CON_2H_4)_5 \cdot H_2O]^{3+} + H_2O = [Cr(CON_2H_4)_4 \cdot (H_2O)_2]^{3+} + CON_2H_4$$

and finally

$$V - [Cr(CON_2H_4)_2 \cdot (H_2O)_4]^{3+} + H_2O = [Cr(CON_2H_4)(H_2O)_5]^{3+} + CON_2H_4.$$

Ions of the $[Cr(CON_2H_4)_n (H_2O)_{6-n}]^{3+}_{(n<6)}$ type are evidently not precipitated by ferrocyanide.

The rate constant obtained by determination of the content of hexaurea chromic salt in the solution vai titration appears to be the rate constant of the first stage of aquatization of the complex salt.

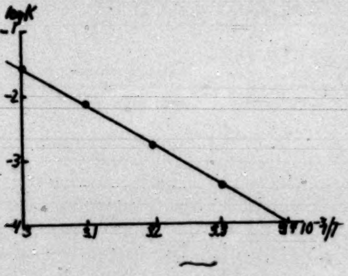

Fig. 2. Dependence of the rate constants of the aquatization reaction on the temperature.

Further displacement by water molecules of urea molecules from the inner sphere should lead to a certain change in the optical density of the solution. Consequently, the values of the rate constants obtained from the optical data, reflect not only the first stage of aquatization of the complex, but also the subsequent stages of this process.

The hypothesis of Kilpatrik concerning complete dislodgement from the inner sphere of urea molecules by water molecules was not substantiated. The aquatization process proceeds in stages and even in the moment of achieving equilibrium, complex ions remain in the solution.

The data obtained by the method of Ostromyslensky-Zhob indicate that the hypothetical composition of the complex appears to be a final product of the decomposition of $[Cr(CON_2H_4)(H_2O)_5]^{3+}$. This compound can be obtained both by destruction of the hexaurea chromic ion by water and by stirring solutions of chromic salt with urea.

Analysis of the temperature dependence of the rate constant of the reactions studied shows that in the given case the Arrhenius equation is rather strictly observed (Fig. 2).

The activation energy at the same time amounts to 13,200 kcal, while log pz = 16.45. The high value of the preexponential factor — pz attracts attention. Such a high value of the preexponential factor for ionic reactions proceeding in aqueous solutions has been observed previously [6]; Bjerrum [7] considered that the high value of the preexponential factor is a peculiarity of the complex formation reactions of numerous ions.

There is no single accepted opinion at the present time regarding the problem of the causes of such a high value for the pz factor.

Using the Arrhenius equation with the obtained constants, we calculated the rate constant of the aquatization of hexaurea chromic ion in aqueous solution for 22.5° and found $1.12 \cdot 10^{-4}$ min^{-1}, Kilpatrik found $1.11 \cdot 10^{-4}$ [5]. Thus, an entirely satisfactory agreement is observed between our data and the value for the constant (for another temperature) obtained previously.

SUMMARY

1. The rate constants of the aquatization reaction of the hexaurea chromic ion in aqueous solution at temperatures of 30, 40, 50 and 60° were measured and shown to be respectively equal to $3.84 \cdot 10^{-4}$, $1.62 \cdot 10^{-3}$, $7.06 \cdot 10^{-3}$ and $2.45 \cdot 10^{-2}$ minutes^{-1}. The activation energy (13,200 kcal) and log pz (16.45) were calculated.

2. The rate of the aquatization reaction of the hexaurea chromic ion was also studied by optical methods. The values obtained for the rate constant maintained a satisfactory constancy, but differed somewhat from those set forth above.

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$$V - [Cr(CON_2H_4)_2 \cdot (H_2O)_4]^{3+} + H_2O = [Cr(CON_2H_4)(H_2O)_5]^{3+} + CON_2H_4.$$

Ions of the $[Cr(CON_2H_4)_n(H_2O)_{6-n}]^{3+}_{(n<6)}$ type are evidently not precipitated by ferrocyanide.

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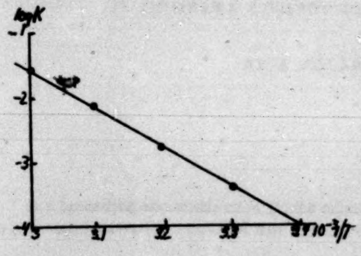

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Analysis of the temperature dependence of the rate constant of the reactions studied shows that in the given case the Arrhenius equation is rather strictly observed (Fig. 2).

The activation energy at the same time amounts to 13,200 kcal, while log pz = 16.45. The high value of the preexponential factor — pz attracts attention. Such a high value of the preexponential factor for ionic reactions proceeding in aqueous solutions has been observed previously [6]; Bjerrum [7] considered that the high value of the preexponential factor is a peculiarity of the complex formation reactions of numerous ions.

There is no single accepted opinion at the present time regarding the problem of the causes of such a high value for the pz factor.

Using the Arrhenius equation with the obtained constants, we calculated the rate constant of the aquatization of hexaurea chromic ion in aqueous solution for 22.5° and found $1.12 \cdot 10^{-4}$ min^{-1}, Kilpatrik found $1.11 \cdot 10^{-4}$ [5]. Thus, an entirely satisfactory agreement is observed between our data and the value for the constant (for another temperature) obtained previously.

SUMMARY

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DETERMINATION OF THE COMPOSITION AND THE INSTABILITY CONSTANTS OF COMPLEX COMPOUNDS BETWEEN METALS AND THIOUREA BY A POLAROGRAPHIC METHOD. II

O. S. Fedorova

In a preceding communication [1] the question was raised as to whether the following sequence of the divalent metal series is maintained with regard to diminishing stability of the thiourea complexes:

$$Hg^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+},$$

as could be expected from consideration of the changes in the covalency in the reactions of complex formation according to the data of Yatsimirsky [2], and as actually takes place for thiosulfate, halide and thiocyanate complexes. Dimensions were given there which characterize the structure and the stability of the thiourea complexes of two members of the above-mentioned series — lead and cadmium. The structure and the stability of the complexes of Zn, Ni, and Bi are considered in the present communication.

According to the data of A. T. Pilipenko and G. S. Lisetskaya [3], the instability constant of the thiourea complex of divalent mercury is equal to 10^{-22} (determined potentiometrically). The complex of divalent copper with thiourea does not exist, since the monovalent ion forms a complex, and therefore copper is excluded from the above-mentioned series. Measurement of the half-wave potentials was conducted under the same conditions and in the same apparatus as in the preceding work.

Zinc. Two series of experiments conducted at different times led to identical results: it was shown that the half wave potential did not depend on the concentration of the addendum. In spite of the fact that from 0.2 to 0.8 mole/liter of the latter was added and its concentration exceeded the concentration of zinc ions by 50-200 times, the magnitude of $E_{1/2}$ remained unchanged within the limits of experimental error (±2 mV). Addition of thiourea to the simple zinc ion in a background of 0.1 N KCl displaced the potential to the opposite side by 10-14 mV, as if a chloride complex of zinc was decomposed, if one considers the action of the "background" as weak complex formation.

TABLE 1

Metal ion	Covalent index	$K_{instability}$
Hg^{2+} . .	228	10^{-22}
Cd^{2+} . .	159	$1.2 \cdot 10^{-3}$
Pb^{2+} . .	156	$1.7 \cdot 10^{-2}$
Zn^{2+} . .	136	Complex absent
Ni^{2+} . .	97	The same and displacement of $E_{1/2}$ to the opposite side

It is thus evident that zinc does not form a complex with thiourea in aqueous solution.

Nickel. While in the case of zinc the displacement under the same concentration of addendum is expressed in tenths of mV, in the case of nickel this displacement amounts to about 200 mV. It is well known from the literature data that such a phenomenon is repeatedly observed. For example, it follows from the data of Kolthoff and Lingane [4] that $E_{1/2}$ of the nickel ion in 1N KCNS is displaced by 400 mV to the opposite side in relation to $E_{1/2}$ of the same ion in 1N KCl. The same thing is observed in the reaction of the nickel ion with pyridine.

It follows from these data that the sequence of the series of metals is preserved, since the stability of these complexes in solution diminishes with decrease in the covalent indices (Table 1).

Bismuth. The complex compound of the trivalent bismuth ion with thiourea has long been utilized both to detect Bi^{3+} and for its quantitative determination.

In agreement with the literature data, in the solid form several different thiourea complexes of bismuth exist.

According to the communication of Babko and Pilipenko [5], the soluble complex with a coordination number of 9 and a dissociation constant of $6.4 \cdot 10^{-2}$ (this was apparently sequential) has the most intense coloration.

In the article of Yatsimirsky and Atasheva [6] there is an indication concerning the preparation of a complex with a coordination number of 6, which is found to be in agreement with the value found in the present work.

The coexistence of several complexes of bismuth with thiourea is entirely possible under various conditions, and the goal of the present work was, consequently, not only to establish the composition of the complexes in aqueous solution, but also to determine the instability constant (general and sequential).

The conditions of the measurements differed from [1] only in the fact that: 1) to avoid hydrolysis, the electrolyte was acidified to pH 0.32; and 2) the bismuth concentration amounted to $2.7 \cdot 10^{-3}$ mole/liter.

The reversibility of the process of discharging the bismuth ion was established from the experimental data accumulated by us.

Actually, from consideration of the equation of the polarographic wave, the tangent of the angle of inclination (at n = 3) is seen to be equal to $\frac{0.059}{3} = 0.0197$, while the mean experimental value is equal to 0.021.

Determination of the composition of the thiourea complex, that is, the coordination number, was conducted by constructing a graph with the coordinates: $E_{1/2}$ − log $c_{CSN_2H_4}$ (Fig. 1), from which it follows that the tangent of the angle of inclination $\frac{\Delta E_{1/2}}{\Delta \log c} = 0.117$, i.e., $p = 5.9 \approx 6$.

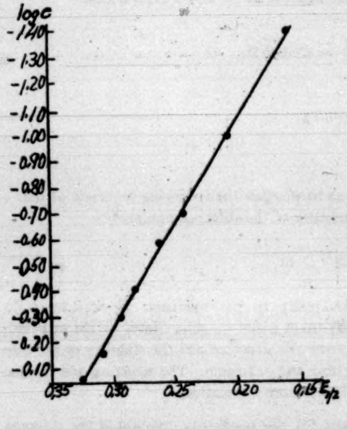

Fig. 1. Curve of the dependence of log·c on $E_{1/2}$ for the determined composition of the thiourea complex.

Evidently, in the range of change of concentration of the addendum of from 0.04 to 0.88 mole/liter, the composition of the complex cation is as follows: $[Bi(CSN_2H_4)_6]^{3+}$.

A shortened form of the well known formula was employed to calculate the instability constant:

$$\Delta E_{1/2} = -\frac{0.0591}{3}\log K_{\text{instability}} + p\,\frac{0.0591}{3}\log c_{CSN_2H_4} \qquad (1)$$

The ratio of the diffusion currents and the activity coefficient of the addendum was taken as unity.

In Table 2 the experimental data and the calculated magnitude of the instability constant are presented. Its mean value was equal to

$$1.09 \cdot 10^{-12} \pm 20\%.$$

Since equation (1) is represented by the straight line y = a − bx, then, using the method of least squares for calculation, it can be reduced to the form:

$$y = 0.2349 + 0.1157x, \qquad (2)$$

whence: $K_{\text{instability}} = 1.2 \cdot 10^{-12}$ and $p = 5.87$.

The results are in entirely satisfactory agreement.

TABLE 2

Experiment No.	$\Delta E_{1/2}$ (in V)	c in moles/liter of thiourea	$K_{inst.} \cdot 10^{-12}$
1	0.076	0.04	0.63
2	0.117	0.10	1.15
3	0.154	0.20	0.9
4	0.172	0.30	1.3
5	0.186	0.40	1.5
6	0.200	0.50	1.2
7	0.218	0.70	1.15
8	0.231	0.88	0.9
		Mean	1.09 ± 20%

The change in the thermodynamic potential in the ionization process can be enumerated from the magnitude of the ionization constant of the complex:

$$\Delta Z = -RT\ 2.3 \log K = 4 \cdot 575 \cdot 298 \cdot 12 = 16360\ \text{cal.}$$

Since the composition and the stability of the bismuth complex can be determined only in acidic medium, it is evident that the acid, in the given case hydrochloric, playing the simultaneous role of background and addendum, will influence the magnitude of the instability constant.

The majority of the measurements were conducted at a pH of around 0.35. Variation of the magnitude of pH up to 6-7% had little influence, since the experimental error depended chiefly on the variation of the magnitude of $E_{1/2}$. During a more significant variation in pH the change in $K_{instability}$ became very noticeable, and with lowered pH the magnitude of the instability constant increased and vice versa. This is explained by the fact that the half wave potential of the complex ion responds less to change in pH than the half wave potential of the simple ion. It is evident from this that at low values of pH, $\Delta E_{1/2}$ is diminished while the instability constant is increased. I express thanks to K. B. Yatsimirsky for providing the subject and valuable counsel.

SUMMARY

1. The successive diminishing of stability with diminishing covalent index of a series of metal ions in combination with thiourea was confirmed.

2. The coordination number (p = 6) and the instability constant ($K_{instability} = 1.1 \cdot 10^{-12}$) of the thiourea complex of bismuth were determined.

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* See Consultants Bureau Translation, page 1461.

** See Consultants Bureau Translation, page 45.

TABLE 3 [illegible]

Experiment	[illegible]	c in moles liter	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

step, with allowance for the magnitude of the [illegible]

The measurement of the [illegible] was conducted at a [illegible] of [illegible]

During a more significant variation in pH the change in [illegible]

[illegible] the magnitude of the [illegible]

It is evident from this that at low values of pH [illegible] is diminished while the [illegible] constant [illegible]

[illegible] K. B. Yatsimirsky for reviewing the subject and valuable counsel.

SUMMARY

1. The increasing [illegible] of [illegible] with diminishing [illegible] constant [illegible]

2. The [illegible] constant [illegible]

[1] [illegible]

[2] K. B. Yatsimirsky, [illegible]

[3] A. T. Pilipenko and [illegible]

[4] I. M. Kolthoff and [illegible] Lingane, Polarography [illegible]

[5] A. K. Babko and A. T. Pilipenko, [illegible]

[6] K. B. Yatsimirsky and [illegible] J. Anal. Chem. [illegible]

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[*] See Consultants Bureau Translation, page [illegible]

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

III. HYDROGENATION OF ACETYLENEDICARBOXYLIC ACID

A. L. Markman

The question concerning the character of the process of saturation of compounds with a triple bond is associated with the problem of the selectivity of the hydrogenation process.

The majority of authors who have conducted the hydrogenation of acetylenic derivatives with a palladium catalyst, have noted the selective character of this process; a selective conversion of the acetylenic compound into an ethylenic proceeds initially, and only in the second instance does conversion of the ethylenic into the corresponding saturated derivative occur. The rate of hydrogenation in the second stage can be greater, equal to, or less than the rate of hydrogenation in the first stage, depending on the functional nature of the compound being hydrogenated.

Bourguel [1] described an experiment involving the catalytic hydrogenation of acetylenedicarboxylic acid in the presence of colloidal palladium and starch as a protective colloid; maleic acid was obtained. Ott and Schröder [2], in a study of the semisaturation products of acetylenedicarboxylic acid, found that during rapid hydrogenation, the sole reaction product was maleic acid, while during slow hydrogenation – fumaric acid was produced, which was apparently a secondary product of the conversion.

In contrast to palladium catalysts, platinum catalysts (platinum black, platinum hydrosols) according to the data of the majority of authors, cause unselective hydrogenation of acetylenic derivatives, characterized by the absence of a break in the rate of the process after half saturation of acetylene. We have not encountered in the literature attempts to hydrogenate acetylenedicarboxylic acid in the presence of platinum.

EXPERIMENTAL

We summarize the data of one experiment of the hydrogenation of acetylenedicarboxylic acid.

0.57 g of acetylenedicarboxylic acid; 105 mg of Al and 32 mg of Pd; and 40 ml of alcohol were taken. The bath temperature was 25°, the air temperature was 26°, the pressure 717 mm; the theoretical absorption of hydrogen H_0 = 260 ml.

τ•	1	2	3	4	5	6	7
V••	7.2	13.2	18.2	23.6	28.6	34.0	38.6
τ	8	9	10	11	12	13	14
V	43.8	48.6	53.0	58.6	63.4	68.4	72.6
τ	15	16	17	18	19	20	21
V	77.2	81.6	85.6	90.2	94.2	97.2	101.4
τ	22	23	24	25	26	27	28
V	105.2	108.8	112.0	115.4	118.4	121.8	124.8
τ	29	30	31	32	33	34	35
V	127.8	130.8	133.8	136.0	138.4	140.8	142.4
τ	36	37	38	39	40	41	
V	144.8	148.0	150.0	152.0	153.8	155.6	
τ	42	43	44	45	46	47	
V	157.6	159.0	160.6	162.0	163.6	165.2	
τ	48	49	50	51	52	53	
V	166.8	168.0	169.4	170.6	172.0	173.2	
τ	54	55	56	57	58	59	
V	174.4	175.8	177.0	178.0	179.0	180.0	
τ	60	61	62	63	64	65	
V	181.0	183.0	184.4	185.6	186.8	187.6	
τ	66	67	68	69	70	71	
V	188.6	189.6	190.6	191.6	192.6	193.4	etc.

•Time in minutes.

••Volume in milliliters.

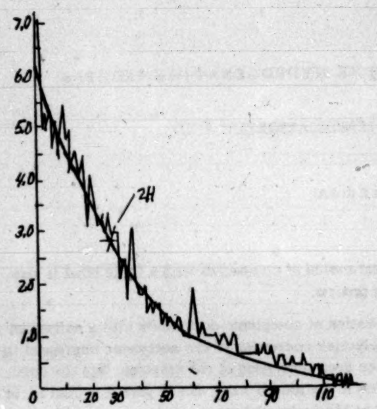

Fig. 1. Curve of the rate of absorption of hydrogen. Explanation in the text.

The curve of Figure 1 is plotted from the data of this experiment; the rate of absorption of hydrogen is plotted on the ordinate (ml/minute). No break in the curve is observed after the absorption of the first 2H: the rate of absorption of hydrogen falls from the first to the last minutes of the process; its fall, at the beginning more rapid, becomes retarded toward the end.

We employed the polarographic analysis method to study the process of catalytic hydrogenation of acetylenedicarboxylic acid as in the preceding work [3].

The methodology of the polarographic investigation of mixtures of acetylenedicarboxylic and maleic acids has been described earlier [4]. The presence of succinic acid as a third component in the mixture does not interfere with the determination of the quantities of the two unsaturated acids, since succinic acid does not give polarographic waves.

We used the single stage method of polarography for which mixtures were employed that were formed at various stages of the hydrogenation in aqueous solutions with a buffered background of 1 N HCl at pH 2.7 and $\underline{t}$ 25°, $\underline{v}$ = 14 drops/minute. Under these conditions the half wave potential of the total wave (maleic acid and the first wave of acetylenedicarboxylic acid) lies at −0.80 V, the second wave of acetylenedicarboxylic acid at −1.15 V. The coefficient of proportionality (between the diffusion current and the concentration) under the indicated conditions was equal for maleic acid, to:

$$\left(\frac{i'_d}{c}\right)_{av.} = 4.76 \cdot 10^3$$

and for the second wave of acetylenedicarboxylic acid,

$$\left(\frac{i''_d}{c}\right)_{av.} = 5.89 \cdot 10^3;$$

the ratio of the magnitudes of the diffusion currents for the first and second waves of acetylenedicarboxylic acid

$$\frac{i'_d}{i''_d} = 0.0407.$$

As a consequence of the small magnitude of this ratio at low contents of acetylenedicarboxylic acid in the mixtures one can, without great error, consider the wave lying at the more positive potential values as the wave of maleic acid.

In addition, the polarographic method was employed with added standard solution.

One series of polarograms obtained from a series of samples removed from the acetylenedicarboxylic acid solution during its hydrogenation is presented in Fig. 2. Curve 1 refers to the initial solution: only one wave is observed on it, that of acetylenedicarboxylic acid. Two waves are observed on Curves 2-6 — all are diminished in the height of the acetylenedicarboxylic acid wave and at a more positive potential all are increased in the total wave of maleic and acetylenedicarboxylic acids. Only one wave is still evident in Curves 7-9, that of maleic acid, the height of which also gradually falls in proportion to the conversion of maleic acid into succinic acid. Finally, in Curve 10, taken after cessation of hydrogen absorption, no waves are observed, since at this time only succinic acid is found in the solution.

Hydrogenations of acetylenedicarboxylic acid and also of mixtures of acetylenedicarboxylic and maleic acids in the presence of palladium and platinum were conducted.

Hydrogenation of Acetylenedicarboxylic Acid

1. Hydrogenation of Acetylenedicarboxylic Acid in the Presence of Palladium. 114 g of acetylenedicarboxylic acid; 210 mg of Al and 64 mg of Pd; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25° and of air 22°, the pressure was 713.5 mm; the theoretical absorption H_0 = 515.6 ml. For the polarography 1.0 ml of each sample was diluted with buffer with a pH of 2.7 to a volume of 50 ml. The half-wave potential: total half waves −0.75 V, second wave of acetylenedicarboxylic acid −1.13 V (Table 1, Fig. 3).

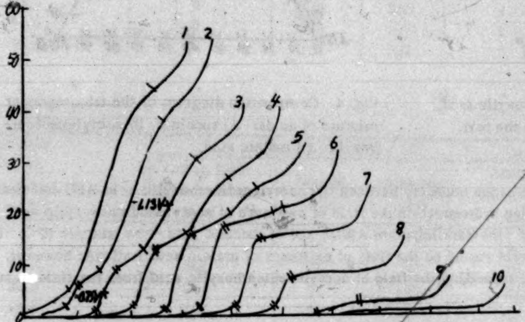

Fig. 2. Series of polarograms of samples of acetylenedicarboxylic acid in the course of hydrogenation. Explanation in the text.

Curve a on Fig. 3 represents the disappearance of acetylenedicarboxylic acid in proportion to the absorption of hydrogen expressed in percentages of the initial quantity; the curve m—the disappearance of maleic acid and the simultaneous accumulation of succinic acid, expressed in percentages of that quantity which would accumulate as a result of complete hydrogenation. Here, the saturation curve during a completely unselective process would coincide with the diagonal AC. During a strictly selective process acetylenedicarboxylic acid would be saturated along the broken line ADC, maleic acid along the broken line ABC. In the given case the degree of selectivity can be measured by the ratio of the area of the figure AaCmA to the area of the parallelogram ABCD. For this case it was found that p_1 = 0.1817, p_2 = 0.1721, S = 0.920.

This same curve characterizing the course of the saturation of acetylenedicarboxylic and maleic acids, can also serve as the curve of the change in composition of the tricomponent mixture (acetylenedicarboxylic-maleic-succinic acid) in the course of hydrogenation. Here 1—the field of existence of acetylenedicarboxylic acid, 3—the field of existence of succinic acid, 2—the field of existence of maleic acid.

TABLE 1

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylenedicarboxylic acid	Maleic acid	Succinic acid	Acetylenedicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100.0	0	0
10.0	400	100	0	80.0	20.0	0
20.3	296	204	0	59.2	40.8	0
31.0	190	310	0	38.0	62.0	0
41.8	107	368	25	21.4	73.6	5.0
53.1	54	361	85	10.8	72.2	17.0
64.5	0	355	145	0	71.0	29.0
76.3	0	237	263	0	47.4	52.6
88.4	0	116	384	0	23.2	76.8
90.0	0	100	400	0	20.0	80.0

Evidently, during a completely unselective hydrogenation, when each molecule of maleic acid, immediately after its formation, would be converted into a molecule of succinic acid, we would not have a field of

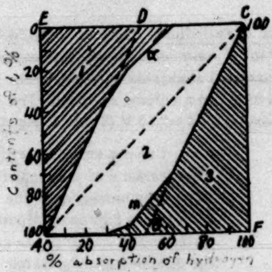

Fig. 3. Hydrogenation of acetylenedicarboxylic acid. Palladium as the catalyst. Explanation in the text.

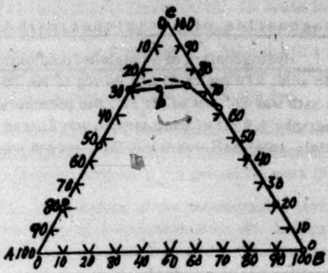

Fig. 4. Composition diagram of the tricomponent mixture of acids: A) succinic, B) acetylenedicarboxylic, C) maleic acid.

maleic acid; the diagonal AC would serve as the boundary between the acetylenedicarboxylic acid AEC and the succinic acid AFC. During strictly selective hydrogenation the field of existence of acetylenedicarboxylic acid would be the triangle AED, of maleic acid – the parallelogram ABCD, and of succinic acid – the triangle BFC. The less selective the hydrogenation, the narrower should be the field of existence of maleic acid AaCmA; however, it will always stretch along the diagonal AC, separating the field of acetylenedicarboxylic acid from the field of succinic acid.

A composition diagram of the tricomponent mixture is presented in a triangular system of coordinates in Fig. 4. The points on the curve of this figure show the composition of samples taken from the duck at various stages of the hydrogenation. The point b corresponds with the initial composition of the product being hydrogenated (100% acetylenedicarboxylic acid). If the process were proceeding strictly selectively, that is, if the acetylenedicarboxylic acid were initially converted into maleic acid and only later, after the disappearance of all the acetylenedicarboxylic acid were the maleic acid converted into succinic, then the change in the composition of the mixture would proceed along the broken line BCA. During a completely unselective hydrogenation or during a selective and preferential saturation of maleic acid, the molecules of this acid at the moment of their formation from half-saturated acetylenedicarboxylic acid would be instantly hydrogenated along with, or preferably before the acetylenedicarboxylic acid, with conversion into succinic acid. In such a case, at any moment of the process we would have a right to expect the presence in the mixture of only two acids – acetylenedicarboxylic and succinic; the change in composition would proceed along the straight line BA.

The character of the process which has been established appears rather highly selective, which agrees with the literature data pertaining to the hydrogenation of acetylenic derivatives and, in particular, of acetylenedicarboxylic acid in the presence of palladium catalyst. Such a character of the process permits us to assume that the maleic acid formed after the half saturation of acetylenedicarboxylic acid is desorbed from the surface of the catalyst and passes into the body of the medium, yielding its place to new molecules of acetylenedicarboxylic acid.

It should be noted that in the first half of the process 5,76% of the initial quantity of acetylenedicarboxylic acid per minute disappears, on the average and 1,10% (of the final quantity) of succinic acid is formed; the first figure characterizes the rate of half saturation of acetylenedicarboxylic acid; the second the rate of saturation of maleic acid; the first quantity is almost 5 times greater than the second.

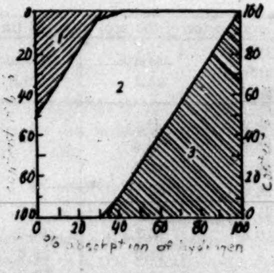

Fig. 5. Hydrogenation of acetylenedicarboxylic and maleic acids. The catalyst was palladium. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

TABLE 2

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	250	250	0	50.0	50.0	0
10.1	174	326	0	34.8	65.2	0
20.4	97	403	0	19.4	80.6	0
30.9	18	482	0	3.6	96.4	0
41.7	0	438	62	0	87.4	12.6
52.7	0	354	146	0	70.8	29.2
64.1	0	270	230	0	54.0	46.0
75.8	0	182	318	0	36.4	63.6
79.5	0	154	346	0	30.8	69.2

TABLE 3

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100	0	0
19.9	392	16	92	78.2	3.2	18.4
34.2	311	34	155	62.2	6.8	31.0
48.5	237	38	225	47.4	7.6	45.0
57.4	187	48	265	37.4	9.6	53.0
60.0	174	48	278	34.8	9.6	55.6

2. Hydrogenation of a Mixture of Acetylenedicarboxylic and Maleic Acids in the Presence of Palladium. 0.57 g of acetylenedicarboxylic and 0.58 g of maleic acid; 210 mg of Al and 64 mg of Pd; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25°, of air 12°, the pressure 734.5 mm; the theoretical absorption H_0 = 363 ml (Table 2).

Although in a given case a significant quantity of maleic acid may be contained in a starting mixture with the same origin, nevertheless, as is evident from Fig. 5, the process proceeds selectively in the first stage at the expense of the preferential half saturation of acetylenedicarboxylic acid. For this experiment the following values were found: p_1 = 0.2343; p_2 = 0.2332; S = 0.995.

The saturation of an equimolar mixture of acetylenedicarboxylic and maleic acids in the presence of palladium is represented in a triangular system of coordinates in Fig. 6. For this the following values were found: p_1 = = 0.1567; p_2 = 0.1558; S = 0.995; that is, the same values as for Fig. 5.

3. Hydrogenation of Acetylenedicarboxylic Acid in the Presence of Platinum. Experiment A. 1.14 g of acetylenedicarboxylic acid; 210 mg of Al and 116 mg of Pt; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25°, of air 26°, the pressure was 715 mm; the theoretical absorption H_0 = 516 ml (Table 3).

The corresponding graph is presented in Fig. 7. p_1 = 0.1845; p_2 = 0.0148; S = 0.080 were found for it.

Since the saturation of acetylenedicarboxylic acid in the presence of platinum did not go to completion in a number of experiments, a hydrogenation experiment was set up at a somewhat higher temperature – at 40° and with a larger quantity of the platinum catalyst.

Experiment B. 1.14 g of acetylenedicarboxylic acid; 420 mg of Al and 232 mg of Pt; 20 ml of alcohol and 20 ml of water were taken. The temperature of the bath was 40° and of air was 15°, the pressure was 723 mm; the theoretical absorption H_0 = 496.8 ml. The conditions of the polarography were analogous to those of the preceding experiment (Table 4).

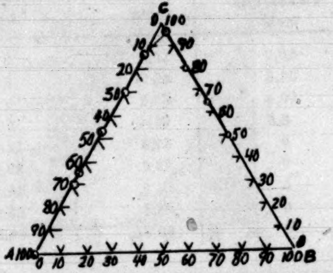

Fig. 6. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic.

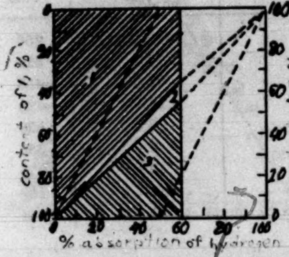

Fig. 7. Hydrogenation of acetylenedicarboxylic acid. Catalyst: platinum. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

TABLE 4

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100	0	0
29.1	330	49	121	66.0	9.8	24.2
42.1	251	77	172	50.2	15.4	34.4
61.4	160	76	264	32.0	15.2	52.8
72.4	103	67	330	20.6	13.4	66.0
76.1	88	59	353	17.6	11.8	70.6

$p_1 = 0.1858$; $p_2 = 0.0354$; $S = 0.190$ were found for the corresponding Fig. 8.

It is noteworthy that the saturation of acetylenedicarboxylic acid (and also of its mixtures with maleic acid) does not go completely in the presence of platinum. It is impossible to explain this phenomenon by a poisoning action of some one of the three acidic components of the reaction mixture: in the first place, the hydrogenation of this very acetylenedicarboxylic acid proceeds completely in the presence of palladium, and, in the second place, the hydrogenation of maleic acid in the presence both of palladium and of platinum also proceeds completely without difficulties. The cause of the indicated phenomenon remains unexplained for us.

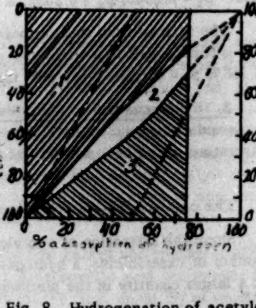

Fig. 8. Hydrogenation of acetylenedicarboxylic acid at 40°. Catalyst: platinum. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

Figures 9 and 10 were plotted in a triangular system of coordinates from the data of the experiments of saturating acetylenedicarboxylic acid in the presence of a platinum catalyst. $p_1 = 0.1724$; $p_2 = 0.0138$; $S = 0.080$, were found for Experiment A; $p_1 = 0.1694$; $p_2 = 0.0329$; $S = 0.190$, were found for Experiment B, that is, exactly the same values for the index of selectivity S as we obtained from Fig. 7 and 8.

As is evident from Figs. 9 and 10, the saturation curves of acetylenedicarboxylic acid lie much closer to the straight line AB than to the broken line ACB. This indicates that the maleic acid formed as a

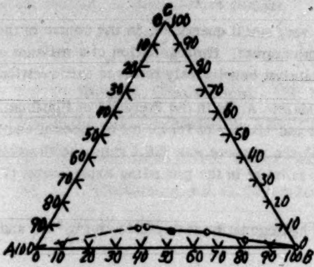

Fig. 9. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic. Catalyst: platinum. At 25°.

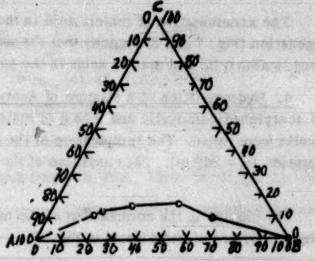

Fig. 10. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic. Catalyst: platinum. At 40°.

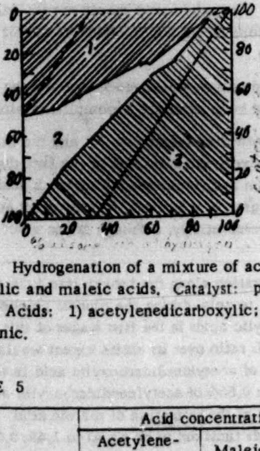

Fig. 11. Hydrogenation of a mixture of acetylenedicarboxylic and maleic acids. Catalyst: platinum. At 40°. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

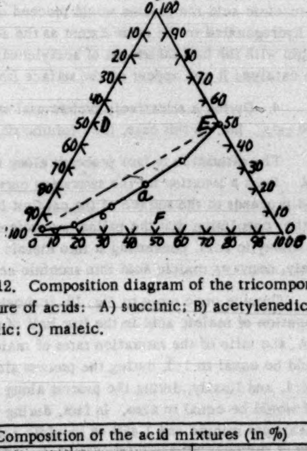

Fig. 12. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic.

TABLE 5

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	250	250	0	50.0	50.0	0
17.6	227	162	111	45.4	32.4	22.22
37.6	176	110	214	35.2	22.0	42.8
54.2	132	62	306	26.4	12.4	61.2
60.5	129	36	335	25.8	7.2	67.0
75.0	72	21	407	14.4	4.2	81.4
90.9	15	10	475	3.0	2.0	95.0

result of the half saturation of acetylenedicarboxylic acid is for the most part instantly further saturated — to succinic acid. Evidently, one can assume that a molecule of acetylenedicarboxylic acid which is not desorbed from the surface of the catalyst after half saturation, then and there reacts with a second hydrogen molecule. On the other hand, one can assume that after half saturation the molecule escapes into the medium and that subsequently, of the two acids found in the reaction media — acetylenedicarboxylic and maleic — maleic acid is preferentially absorbed and hydrogenated on the surface of the platinum.

The accumulation of maleic acid in the medium, although in very small quantities, in the course of the hydrogenation (Fig. 7 and 8) suggests that the second explanation is more correct. Hydrogenation of a mixture of acetylenedicarboxylic and maleic acids in the presence of a platinum catalyst conclusively resolved this question.

4. Hydrogenation of a Mixture of Acetylenedicarboxylic and Maleic Acids in the Presence of Platinum. 0.57 g of acetylenedicarboxylic and 0.58 g of maleic acids; 420 mg of Al and 232 mg of Pt; 20 ml of alcohol and 20 ml of water were taken. The temperature of the bath was 40°, of air 14°, the pressure was 726.5 mm; the theoretical absorption H_2 = 369 ml. The conditions of the polarography were the same as in the preceding experiments (Table 5).

The change in the composition of the mixture in the course of hydrogenation is depicted in Fig. 11, and in a triangular system of coordinates in Fig. 12.

Let us consider what character Fig. 12 would have during various possible directions of the process.

1. During selective half saturation of acetylenedicarboxylic acid, as it occurs in the presence of palladium, the process would proceed along the broken line ECA.

2. During selective saturation of acetylenedicarboxylic acid into succinic (without desorption of the maleic acid formed as an intermediate) the process would proceed along the broken line EDA.

3. During an absolutely unselective hydrogenation of both unsaturated acids with the conversion of both into succinic acid the process would proceed along the straight line EA. But this means that, in order that it should be hydrogenated to the same extent as the acetylenedicarboxylic acid, the maleic acid should not be linked by its origin with the half saturation of acetylenedicarboxylic acid, and therefore should not be bound by the surface of the catalyst; it can appear on the surface from the body of the medium.

4. During a selectively preferential saturation of maleic acid the process would proceed along the broken line DFA. But, in this case, the "volumetric origin" of maleic acid had been certainly accomplished already.

The saturation in fact proceeds along the curve EaA, lying between the straight line EA and the broken line EFA. Such a location for the saturation curve in the first place conclusively persuades one of the fact that maleic acid proceeds to the surface of the catalyst from the body of the medium and, in the second place, it leads to the similar conclusion that the palladium preferentially and with a high degree of selectivity hydrogenates acetylenedicarboxylic acid, converting it into maleic acid, and that platinum preferentially, although not so strictly selectively, converts maleic acid into succinic acid.

Turning once more to Fig. 12, it should be noted that during saturation along the broken line ECA the rate of saturation of maleic acid in the first half of the process would be equal to zero; during the process proceeding along EDA, the ratio of the saturation rates of maleic and acetylenedicarboxylic acids in the first stages of this process would be equal to 1:1, during the process along the straight line EA this ratio over its entire extent would be equal to 2:1, and finally, during the process along EFA the rate of saturation of acetylenedicarboxylic acid in the first half would be equal to zero. In fact, during the first half of the process 0.55% of acetylenedicarboxylic acid disappears per minute and 1.42% of succinic acid is formed at the expense of the saturation of maleic acid. Thus, the ratio of the rates of saturation of maleic and acetylenedicarboxylic acids turns out to be equal to 1.42:0.55 = 2.6:1, which causes the saturation curve to take a position between EA and EFA.

SUMMARY

1. It was established that acetylenedicarboxylic acid is hydrogenated in the presence of palladium at a rate which gradually falls from the beginning to the end without a break in the curve after the absorption of the first two hydrogen atoms.

2. During the hydrogenation in the presence of palladium, acetylenedicarboxylic acid in the first stage is almost completely converted into maleic acid and only in the second stage is maleic acid hydrogenated into succinic acid; the process is of a strictly selective nature. In the presence of platinum the acetylenedicarboxylic acid is at once hydrogenated to succinic acid with, however, the simultaneous formation of small quantities of maleic acid. In mixtures of acetylenedicarboxylic and maleic acids in the work with palladium in the first stage, the half saturation of acetylenedicarboxylic acid proceeds almost strictly selectively; in the work with platinum in the first stage, maleic acid is saturated, although not strictly selectively. It was established that during the

hydrogenation of acetylenedicarboxylic acid in the presence of either catalyst, the maleic acid formed in the course of the process is desorbed and escapes into the body of the medium, whence it is subsequently once more adsorbed, possibly on other active centers.

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[illegible] in the presence of water [illegible] formed on the surface of the [illegible] is desorbed and passes into the body of the medium, whereas it is [illegible] adsorbed, possibly on other active centers.

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THE HYDROGEN BOND AND THE DENSITY OF SOLUTIONS

A. E. Lutsky

In benzene solutions a dissolved substance that is capable of forming hydrogen bonds as a rule preserves its tendency toward association due to the hydrogen bonds between the molecules; in alcohol, however, as is supposed [1], association between the molecules of the same substance in the majority of cases diminishes the association with the solvent molecules. In either case the extent to which association of the molecules influences the density of the solutions is of interest.

To detect the influence of association one must first of all exclude or take account of the influence of other properties of the molecule, such as mass and size, on the density. This can be achieved according to a well-known method, by comparison of the density of the solutions samples of identical weight dissolved in identical volumes of solvent. In fact, the density of the solution $d = m_1n_1 + m_2n_2$, where m_1 and n_1 are the mass and number (per unit volume of the solution) of the molecules of the dissolved substance, m_2 and n_2 the mass and number of molecules of the solvent. In the solutions indicated above, m_1n_1 are identical for various substances. The greater the value of n_2, the less is n_1 and the molecular size of the dissolved substance and the greater the coupling forces of the molecules of the dissolved substance between each other and with the solvent molecules. Inasmuch as the molecular size in an enormous number of compounds varies parallelly with their masses, its influence on n_2 is to a considerable extent compensated for by the influence of n_1. As a result, the difference in n_2 and, hence, in the value of the density of such solutions, should, evidently, chiefly determine the differences in the coupling forces (including hydrogen bonds) of the molecules of the solute between themselves and with solvent molecules.

To answer the question raised above, the values of the density of solutions of the indicated type in benzene and alcohol at 50° of 42 compounds were determined and are summarized in Tables 1, 2, and 3. As follows from the data summarized in the tables, in the case of solutions of monosubstituted benzenes, the functional groups are arranged in series according to the value of the density of the solutions:

for solutions in benzene – $NO_2 > COOH > OH \approx COCH_3 > CHO > OCH_3 > CH_3$;

for solutions in alcohol –

$$COOH \approx NO_2 > OH > CHO > COCH_3 > COOC_2H_5 > OCH_3 > CH_3.$$

As was expected, the functional groups with the greater group moment and hence with greater coupling forces give solutions of higher density. These groups are arranged in the series on the basis of the group moments corresponding to them. Only phenol and particularly benzoic acid give solutions of appreciably higher density than follows from their group moment.

The density of a solution of phenol in benzene and alcohol is appreciably higher than that of the corresponding solutions of anisole. This was also observed in the case of the methyl ethers of the cresols and of the m- and p-isomers of various substituted phenols. At the same time the magnitude of the reduction in the density in the case of the ethers in comparison with the density of the initial hydroxy compounds was almost the same in all cases: in benzene it varied between 0.0025-0.0036, and in alcohol between 0.0022-0.0031. This same thing was observed in the case of solutions of acids, the ethyl esters of which yield solutions with a density 0.0040 (in alcohol) and 0.0036 (in benzene) less than the corresponding acids.

Solutions of metameric compounds not containing the hydroxyl group (for example, anisole and the m- and p-methoxybenzaldehydes), possess both in benzene and in alcohol a lower density than solutions of the corresponding

TABLE 1

Density of Solutions in Benzene at 50° ± 0.1° (Weighed Portions of 0.9984-0.9990 g in ~25 ml of Solution

Compound		d_4^{50}	Difference in the density of the solution		
			$d_m - d_o$	$d_p - d_o$	$d_{OCH_3} - d_{OH}$
Nitrobenzene		0.8593	–	–	–
Nitrophenol:	o-	0.8603	–	–	–
	m-	0.8636	+0.0033	–	–
	p-	0.8639	–	+0.0036	–
Nitroanisole:	o-	0.8609	–	–	+0.0006
	m-	0.8603	−0.0006	–	−0.0033
	p-	0.8603	–	−0.0006	−0.0036
Benzaldehyde		0.8552	–	–	–
Acetophenone		0.8557	–	–	–
Hydroxyacetophenone:	o-	0.8570	–	–	–
	m-	0.8588	+0.0018	–	–
	p-	0.8591	–	+0.0021	–
Methoxyacetophenone:	o-	0.8560	–	–	−0.0010
	m-	0.8560	0.0000	–	−0.0028
	p-	0.8563	–	+0.0003	−0.0028
Toluene		0.8462	–	–	–
Cresol:	o-	0.8537	–	–	–
	m-	0.8532	−0.0005	–	–
	p-	0.8536	–	−0.0001	–
Cresylmethyl ether:	o-	0.8511	–	–	−0.0026
	m-	0.8507	−0.0004	–	−0.0025
	p-	0.8509	–	−0.0002	−0.0027
Phenol		0.8556	–	–	–
Anisole		0.8528	–	–	−0.0028

TABLE 2

Density of solutions of substituted benzoic acids and derivatives of benzoic acid in benzene and alcohol at 50° ± 0.1° (weighed portions of 0.9990-0.9994 and 0.5000 g in 25 ml of solution).

Compound		d_4^{50} (in benzene)	d_4^{50} (in alcohol)	Difference in density of the solutions in alcohol	
				$d_p - d_o$	$d_{OR} - d_{OH}$
Benzoic acid		0.8574	0.7918	–	–
Ethyl benzoate		0.8538	0.7875	–	−0.0043
Hydroxybenzoic acid:	o-	–	0.7939	–	−0.0039
	m-	–	0.7956	–	−0.0042
	p-	–	0.7960	+0.0021	−0.0039
Methoxybenzoic acid:	o-	0.8528	0.7934	–	−0.0005
	p-	–	0.7936	–	−0.0024
Ethyl hydroxybenzoate:	o-	0.8509	0.7900	–	–
	m-	0.8514	0.7914	–	–
	p-	0.8519	0.7921	+0.0021	–
Ethyl methoxybenzoate:	o-	0.8510	0.7892	–	−0.0008
	p-	0.8514	0.7899	+0.0007	−0.0022

metamers containing the hydroxyl group (cresols, m- and p-hydroxyacetophenones).

That the indicated peculiarities were expressly evoked by a tendency toward the formation of hydrogen bonds between the molecules is indicated by the behavior of compounds studied with an intramolecular hydrogen bond such as the o-hydroxy-substituted nitrobenzene, benzaldehyde, acetophenone, benzoic acid and its ethyl ester. All these compounds preserve their tendency toward the formation of hydrogen bonds within the molecules in benzene

TABLE 3

Density of Solutions in Ethyl Alcohol at 50° ± 0.1° (Weighed Portion of 0.9980-0.9992 g in ~25 ml of Solution

Compound		d_4^{50}	Difference in the density of the solution		
			$d_m - d_o$	$d_p - d_o$	$d_{OCH_3} - d_{OH}$
Nitrobenzene		0.7918	—	—	—
Nitrophenol:	o-	0.7948	—	—	—
	m- . . .	0.7958	+0.0010	—	—
	p-	0.7959	—	+0.0011	—
Nitroanisole:	o-	0.7937	—	—	−0.0011
	m- . . .	0.7935	−0.0002	—	−0.0023
	p-	0.7933	—	−0.0004	−0.0026
Benzaldehyde		0.7887	—	—	—
Hydroxybenzaldehyde:	o-	0.7910	—	—	—
	m- . . .	0.7938	+0.0028	—	—
Methoxybenzaldehyde:	o-	0.7915	—	—	+0.0005
	m- . . .	0.7908	−0.0007	—	−0.0030
	p-	0.7910	—	−0.0005	—
Acetophenone		0.7880	—	—	—
Hydroxyacetophenone:	o-	0.7898	—	—	—
	m- . . .	0.7919	+0.0021	—	—
	p-	0.7925	—	+0.0027	—
Methoxyacetophenone:	o-	0.7892	—	—	−0.0006
	m- . . .	0.7895	+0.0003	—	−0.0024
	p-	0.7895	—	+0.0003	−0.0030
Toluene		0.7813	—	—	—
Cresol:	o-	0.7890	—	—	—
	m- . . .	0.7884	−0.0006	—	—
	p-	0.7887	—	−0.0003	—
Cresylmethyl ether:	o-	0.7859	—	—	−0.0031
	m- . . .	0.7862	+0.0003	—	−0.0022
	p-	0.7857	—	−0.0002	−0.0030
Phenol		0.7896	—	—	—
Anisole		0.7865	—	—	−0.0031

and, to a considerable extent, lack of capacity of forming complex molecules at the expense of the hydrogen bonds between them. As a result solutions of this sort of compound, in spite of the presence of the hydroxyl group, conduct themselves in a normal fashion. The density of the solutions of their methyl ethers, as a rule, differs in value from the density of the initial hydroxy compound only in the fourth place (in either direction). The density of a solution of o-methoxybenzaldehyde in alcohol, in contrast to what was observed in the case of the m- and p-isomers, is higher than the density of a solution of the metameric o-hydroxyacetophenone.

The absence of intermolecular association in the o-hydroxy compounds and its presence in their m- and p-isomers is explained by the unusual difference in the values of the density which is observed for solutions of isomers of the compounds under consideration. While the densities of the solutions of all three isomers of the unassociated methyl ethers or the cresols associated to an equal extent, differ from each other in either direction in the fourth place, in the case of the hydroxy compounds set forth above the density of a solution of the same concentration of the o-isomer is always less than that for their m- and p-isomers by 0.0018-0.0036 in benzene and 0.0010-0.0028 in alcohol.

Thus, both in benzene and in alcohol, in spite of the assumed difference in the character of the association, the formation of complexes between the molecules exhibits an identical influence on the density of the solutions not only qualitatively, but also for the most part quantitatively. This can be explained by the fact that in alcohol in the comparatively concentrated solutions studied by us complexes participate in the association with the solvent molecules, but not solitary molecules of this substance. In other words, complexes of the dissolved substance are evidently not completely destroyed in alcohol under the considered conditions. Complete destruction of intramolecular hydrogen bonds is also absent in alcohol.

All the above established relationships for the density of solutions of various compounds in benzene and alcohol (and, according to certain data [2], they are also observed in such a solvent as amyl acetate) are similar to those which are observed for the individual substances in the liquid state. This permits us to determine the presence and character of association of the dissolved substance according to the density of the solutions of the corresponding compounds. The study of association of dissolved substance by the density of its solutions is particularly suitable for those organic compounds which readily undergo decomposition during fusion and in the liquid state, for example, for carboxylic acids of the aromatic series. Thus, the data summarized above for the density of solutions of hydroxy- and methoxybenzoic acids (Table 2) permit us to assume that in alcohol (and not only in benzene) salicylic acid conducts itself simultaneously as a compound with intramolecular hydrogen bonding and as an intermolecularly associated compound of the benzoic acid type; and that p-hydroxybenzoic acid is associated intermolecularly in two ways in alcohol: on the model of benzoic acid through the carboxyl group and on the model of the phenols through the hydroxyl group.

EXPERIMENTAL

The substances studied were synthesized and purified by methods described in the literature. The solvents were purified in the following way: pure benzene was treated with concentrated sulfuric acid, washed with solutions of alkali and water and then dried over calcium chloride; the dried benzene was redistilled in a column (1.5 meter), dried over metallic sodium and again redistilled in a column with a height of 1 meter. The alcohol was prepared by fractionally distilling rectificate in a column, steeping it over unslaked lime, with subsequent twofold redistillation.

The density was measured in a 25 ml pycnometer. The pycnometer was calibrated with benzene. The density of pure solvent d^{50}_4 was taken for benzene to be equal to 0.8464, and for alcohol to be equal to 0.7778. The temperature of 50° was chosen because of the low solubility of the p-hydroxy isomers in benzene. A glass vessel about 20 liters in capacity served as thermostat.

The density values presented in the tables are the averages of several determinations which did not differ from each other by more than 3 units in the fourth place.

SUMMARY

1. The densities at 50° of solutions of 38 compounds in benzene and 42 compounds in ethyl alcohol were determined.

2. It was established that the same relationship of the densities of unassociated and associated inter- and intramolecular compounds as is observed for the individual substances in the liquid state is maintained in benzene and alcohol.

3. The data for the density of solutions can be utilized for the qualitative determination of the presence and character of the association of a dissolved substance.

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PHYSICO-CHEMICAL ANALYSIS OF THE NITRIC ACID – ACETIC ACID SYSTEM

ATOMIC CONCENTRATION AND CORROSIVE PROPERTIES OF THE SYSTEM

A. V. Titov

A systematic study of the nitric acid–acetic acid system was conducted for the first time by Pictet [1], who proved that during the mixing of 2 moles of CH_3COOH with 1 mole of HNO_3 at 127-128°C a compound of the composition $HNO_3 \cdot 2CH_3COOH$ distils without decomposition, and who, among other things, showed the practical interest attaching to the giving system as a means for obtaining other nitration products in addition to those obtained by the usual nitration mixture. In recent years, the study of the given system has also been of interest from the point of view of the new theory of acids and bases of Hantzsch, Bronsted and Usanovich [2].

In 1940 Usanovich and Abidov [3], in a study of the nitric acid–acetic acid system as a nitration mixture, brought out a number of its peculiarities relative to the ordinary nitrating mixture (nitration of side chains and others). In recent years there has appeared a number of works of Miskidzhyan and Trifonov with their co-workers [4], who studied seven physico-chemical properties of the given system (fusibility, viscosity, density, refraction, surface tension, electrical conductivity and heat of solution). As a result of the study of the diagrams of fusion and viscosity, the system was shown to contain a chemical compound of the composition $HNO_3 \cdot CH_3COOH$. The study of the density was of a subsidiary character – the density was measured to estimate the internal friction, and these measurements were insufficiently precise. The study of the surface tension isotherm, the refractive index and the electrical conductivity of the system also did not enable the authors to confirm the presence of the chemical compound of Pictet; on the contrary, all the methods of investigation employed by the authors led to the conclusion that there was present in the solution a chemical compound of another composition, to wit: $HNO_3 \cdot CH_3COOH$.

Zaslavsky [5] in a number of his works, theoretically and experimentally demonstrated the possibility of utilizing the method of atomic concentrations for the physico-chemical study of systems of variable composition. If, during mechanical mixing of two bodies, the magnitude of the atomic concentration appears to be a linear function of the composition (in percentages by volume), then the chemistry taking place during the reaction of the substances always coincides to a greater or lesser degree with the deviations from additivity of the volumetric concentrations. The usual maximum ΔA corresponds to that composition of the new chemical compound which is formed as a result of the reaction of the mixed components, independently of the fact that this compound may also be found in a state of partial dissociation in the initial components.

Borodachev, in an experimental study of the atomic concentrations of the system under consideration, also enumerated the value of ΔA according to the data of Miskidzhyan and Trifonov and showed that they had determined the specific gravity with insufficient precision. Consequently, to calculate the corresponding values of the atomic concentration, we undertook a special determination of the specific gravities of the mixtures. The corrosive properties of the system were simultaneously studied.

The preparation of chemically pure nitric acid was conducted according to Mishchenko's method [6]. The acid which was collected in the receiving flask had a very faint light lemon-yellow color; d_4^{25} 1.5064.

The acetic acid was prepared by twofold fractional crystallization of glacial acetic acid and subsequent threefold redistillation at 117° (754 mm); d_4^{25} 1.0493;

Atomic Concentration

The specific gravities of the mixtures were determined with a pycometer with a ground glass stopper and a capillary in a thermostat at 25°.

The observed specific gravities and the calculated values of the atomic concentrations of the mixtures are set forth in the table, where $d_{exp.}^{25}$ is the experimental specific gravity of the system and $d_{av.}$ is the calculated average value, $\Delta d = d_{exp.} - d_{av.}$, A and $A_{av.}$ are the experimental and calculated average atomic concentrations of the mixture, $\Delta A = A - A_{av.}$.

The small magnitude of the maximum values of ΔA is evidence of the insignificant chemical reaction between HNO_3 and CH_3COOH and the small stability of the compound obtained.

TABLE

Density of the system HNO_3—CH_3COOH and corrosion of steel in this system

Volumes %		$d^{25}_{exp.}$	$d_{av.}$	Δd	A	$A_{av.}$	ΔA	Loss in weight of sample (in g)	Loss in weight of sample (in g/me per 24 hr)
HNO_3	CH_3COOH								
0	100	1.0482	—	—	139.64	139.64	0	0.0663	207.2
10	90	1.1059	1,0939	0.0120	139.13	137.62	1.51	0.0120	37.5
20	80	1.1579	1.1396	0.0183	137.77	135.60	2.17	0.0017	5.3
30	70	1.2068	1.1853	0.0215	136.00	133.58	2.42	0.0007	2.3
40	60	1.2538	1.2310	0.0228	133.99	131.56	2.43	0.0007	2.1
50	50	1.3015	1.2767	0.0248	132.05	129.54	2.41	0.0007	2.2
60	40	1.3427	1.3224	0.0203	129.47	127.51	1.96	0.0013	4.0
70	30	1.3858	1.3682	0.0176	127.11	125.49	1.62	0.0019	5.9
80	20	1.4270	1.4139	0.0131	124.62	123.47	1.15	0.0023	7.2
90	10	1.4652	1.4596	0.0056	122.00	121.45	0.55	0.0034	10.6
100	0	1.5053	—	—	119.43	119.43	0	0.0050	15.6

The maximum ΔA corresponds to a compound of the composition $HNO_3 \cdot CH_3COOH$. This maximum was diffuse; evidently the mutual reaction of the components of the system does not go to conclusion and the following equilibrium is established between the components of the system and the compound being formed:

$$HNO_3 \cdot CH_3COOH \rightleftharpoons HNO_3 + CH_3COOH.$$

Our data, obtained by the method of atomic concentrations, are in agreement with the conclusions of Miskidzhyan and Trifonov.

Corrosive Properties of the System

After determination of the specific gravities of the prepared mixtures, they were used for the study of corrosive properties. About 50 ml of the mixture was poured into containers having capillaries in the lid. The containers were kept in a water thermostat for 2 hours at 25°. At the expiration of the indicated period a preliminarily prepared and weighed sample in the form of plates of dimensions 10 x 10 x 3 mm was dropped into the mixture.

The material of the plates was steel "2", containing 0.1% C, 0.41% Mn, 0.18% Si, 0.03% S, 0.033% P.

After 24 hours the steel samples were taken from the mixture, carefully and quickly washed with a large quantity of distilled water, with alcohol and ether and dried, after which they were weighed. We judged the corrosive action of the mixture by the loss in weight of the sample per 1 square meter of surface.

The results of our investigations are summarized in the last column of the table.

The corrosion of steel in mixtures of nitric and acetic acids is variable. The maximum loss in sample weight occurs in chemically pure CH_3COOH. In the subsequent mixtures with increase in HNO_3 content, the corrosion of steel is diminished, reaching a minimum at a HNO_3 content in the mixture of 40-50% (by volume); during further increase in HNO_3 content in the mixture the corrosion of the steel again gradually begins to increase and in chemically pure acid the loss in weight reaches a quantity of 15.6 g/m^2 per 24 hours.

Thus we see that the minimumloss in weight of the steel sample occurs in a mixture the composition of which corresponds to the compound $HNO_3 \cdot CH_3COOH$. The study of the corrosion properties of the system HNO_3—CH_3COOH furnishes yet another demonstration of the existence of the chemical compound $HNO_3 \cdot CH_3COOH$ in the system.

SUMMARY

1. The specific gravities of mixtures in the nitric acid — acetic system were determined at 25°.

2. The corrosive properties of the mixtures were studied [the losses in weight of steel samples (in grams) per square meter of surface per 24 hours were determined].

3. The presence in the system of a slightly stable compound $HNO_3 \cdot CH_3COOH$ was established by the data concerning the changes in deviations of the atomic concentrations (ΔA) from the calculated averages and the corrosive properties of the mixtures.

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INVESTIGATION OF THE SYSTEM: TETRANITROMETHANE – BENZENE BY VARIOUS PHYSICO-CHEMICAL ANALYTICAL METHODS

B. V. Ioffe and L. S. Lilich

Attention has frequently been directed to the fact that for the correct interpretation of the results of physico-chemical analysis, it is necessary to subject the system under investigation to thorough study and to make use of diverse methods. Complex investigation of systems by various methods of physico-chemical analysis is necessary to elucidate the possibilities of each of these methods and the conditions for their most effective and efficient applications.

However, materials for the comparison of the results of various methods of physico-chemical analysis have as yet been collected to an insufficient extent, and, in particular, there is little in the way of data for the comparative evaluation of the rapidly developing spectrophotometric method. The experimental material available concerning the absorption of light in solutions is very poor as regards complete data for binary liquid systems over the entire concentration range.

At the same time, for the comparison of spectrophotometry with other methods of physico-chemical analysis, it is particularly desirable to accumulate complete data specifically concerning binary systems.

We primarily selected the classical methods of the melting point diagram and the viscosity diagram for this comparison. In addition, as a special problem, we set up the comparison of spectrophotometric and refractrometric data. The general nature of the physical causes evoking the phenomena of the absorption and refraction of light renders such a comparison very interesting and necessary for the determination of the role of the various factors influencing the form of the isotherm of the index of refraction.

We adopted the system: tetranitromethane – benzene as the subject of investigation; a system suitable for the study of various properties over the entire concentration range, and remarkable for the phenomenon of an intense yellow coloration obtained by mixing the colorless components. A similar coloration appears when tetranitromethane is mixed with many anionic organic compounds. The colorimetric study of this phenomenon has been the subject of several works [1, 2], which, as a rule, were conducted in ternary systems (in the presence of solvent) and apart from the investigation of other physico-chemical properties.

Only data concerning the density and surface tension at 25° [3] of the binary system under consideration are available in the literature; they were obtained in connection with the problem of calculating the parachor of methane derivatives, and were not interpreted with the object (of interest to us) of comparing the various physico-chemical analytical methods.

EXPERIMENTAL

Tetranitromethane was synthesized by the action of nitric acid on acetic anhydride [4, 5]. The product obtained by this method melted at 10-12°; neither by the steam distillation recommended for its purification nor by repeated fractional crystallization did we succeed in raising the melting point above 12.2°. A very effective method of purifying the tetranitromethane was treatment with concentrated sulfuric acid (half volume during energetic agitation for several minutes) with subsequent washing with water, drying, and a single crystallization. The product purified by this method had a m.p. of 13.9°, that is, much higher than that achieved via the more complicated repeated redistillation in a vacuum over phosphoric anhydride [6]. Comparison of the constants of our preparation with the best literature data (see Table 1) makes evident its higher degree of purity.

The benzene was the same as that used by one of us during the investigation of the dispersion of hydrocarbon mixtures [7].

The solutions were prepared in a quantity of 20-30 g in a small flask with a ground stopper; a sample weighed to an accuracy of 1 mg of the less volatile tetranitromethane was taken first. As a rule, immediately after preparing the mixtures, the viscosity, refractive indices and density were determined, after which the spectrophotometric and cryoscopic measurements were made in the same day.

TABLE 1

Constants of tetranitromethane

Properties	Preparation employed in present work	Literature data
Melting point	13.9°	13.8 [6]; 13.5 [3]
Density: d_4^{20}	1.6394	1.637* [8]; 1.638 [3]
d_4^{25}	1.6306	1.630 [6]; 1.629 [3]
Refractive index		
n_D^{20}	1.4384	1.4384 [6]
n_D^{25}	1.4360	1.4358 [6]
n_C^{20}	1.4350	1.4349 [8]*
n_C^{25}	1.4327	–
Mean dispersion		
Δ_{FC}^{20}	120.8	120.5* [8]
Δ_{FC}^{25}	120.4	–

The density was determined in a Biron pycnometer in a volume of about 12.5 ml. The d_4^{20} values in Table 3 refer to a vacuum and are precise to $1 \cdot 10^{-4}$ g/ml.

The viscosity was measured with an Ostwald viscosimeter of the usual type (diameter of the capillary ~0.4 mm) calibrated with benzene, the viscosity of which was taken as equal to 0.648 centipoise [9].

The refractive indices were measured for the sodium D line and the two C and F hydrogen lines on a Pulfrich refractometer (the latest prewar Zeiss model).

The measurements indicated were conducted in a thermostat with a temperature variation of not more than ± 0.02-0.03°.

The melting point was determined with an ordinary mercury thermometer with an accuracy of 0.1° by the cooling curve method.

The spectrophotometric measurements were conducted on a Beckmann model quartz spectrophotometer.

Closed cuvettes with quartz aperture of length 1 and 0.5 cm were used. (All the magnitudes for the optical densities on the figures are converted to a length of 1 cm.) A hydrogen lamp was the light source. The aperture width in all measurements was identical. The control cuvettes were filled with water. The average accuracy of the measurements was to 1% of the transmission.**

Results of the Investigation and Discussion of Them

The melting point diagram of the system under study (Fig. 1) is characterized by the presence of a simple eutetic and, consequently, does not yield any evidence of compound formation.

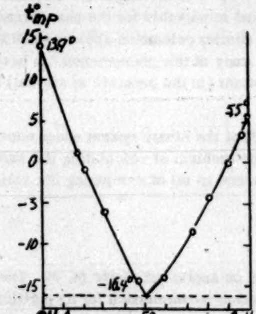

Fig. 1. Melting point diagram of the system: tetranitromethane – benzene.

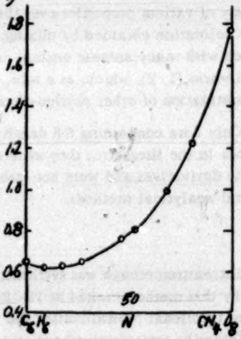

Fig. 2. Viscosity isotherm of the system: tetranitromethane – benzene at 20°

The viscosimetric data (Table 2) are found to be in agreement with the results of the thermal analysis. As is evident from Fig. 2, the viscosity isotherm η^{20} has a minimum which, although not very profound, is clear and is found outside the limits of possible experimental error. Such a form of the viscosity isotherm is encountered in systems with dissociation of an associated component. Viscosity minima are not observed in irrational systems of organic substances [10]. N. A. Trifonov [11, 12], in classifying the isotherms of viscosity and surface tension of binary

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* Calculated from the data for 16.9° using the temperature coefficients found by us.

** M. E. Mogilev participated in the spectrophotometric measurements.

TABLE 2

Viscosity of the system:
tetranitromethane – benzene at 20°

Content of benzene in mol. % (N)	Viscosity η^{20} (centipoises)
0	1.770
18.58	1.225
30.28	0.997
46.33	0.808
52.59	0.759
71.48	0.648
81.60	0.630
90.93	0.626
100	(0.648)

systems, does not exclude the possibility of the existence of minima in irrational systems, taking into account the formal possibility of any ratio between the magnitudes of the properties of the components and of the compound. These formal considerations, however, are certainly insufficient to cause one, solely on the basis of the form of the viscosity isotherm, to doubt that the system: tetranitromethane – benzene is irrational.

There is also a minimum on the surface tension isotherm, as is evident on Figure 3, plotted from the literature data [3]. The comments on the form of the viscosity isotherm set forth above are entirely applicable to the surface tension isotherm of the system being studied.

During the mixing of tetranitromethane with benzene a rather significant increase in volume (Table 3) is observed – a phenomenon which is usual in mixtures of chemically non-reacting substances. The deviations of the molar volume from additivity in the given system do not obey Biron's equation $\Delta M\underline{v} = KN_1N_2$ [13]: the coefficient K is not constant and depends on the concentration, as shown in Fig. 4. Recently, however, it has been noted [14], that Biron's equation is not observed in certain normal systems with markedly different molecular weights of the components, which is exactly what takes place in the given case. The expansion in the system under study is compared with the expansion in mixtures of benzene with saturated hydrocarbons in Fig. 5. It is easy to see that neither in the magnitude of the change in volume observed, nor in its dependence on the concentration of the system $C(NO_2)_4$–C_6H_6 does it in principle differ from mixtures of hydrocarbons.

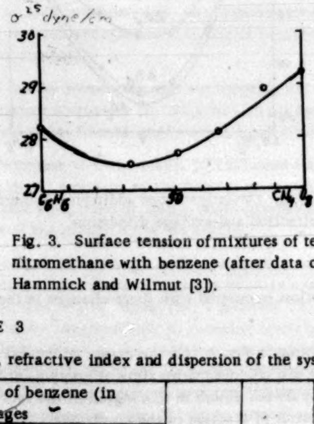

Fig. 3. Surface tension of mixtures of tetranitromethane with benzene (after data of Hammick and Wilmut [3]).

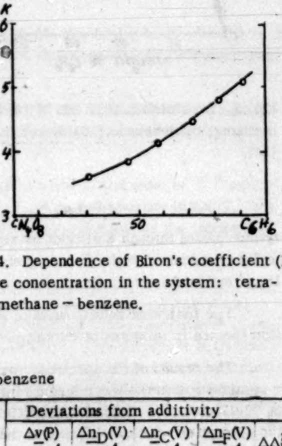

Fig. 4. Dependence of Biron's coefficient (K) on the conoentration in the system: tetranitromethane – benzene.

TABLE 3

Density, refractive index and dispersion of the system: tetranitromethane – benzene

Content of benzene (in percentages)			d_4^{20}	n_D^{20}	n_C^{20}	Δ_{FC}^{20}	ω_{FCD}^{20}	Deviations from additivity				
Gravimetric P	Volumetric V	Molar N						$\Delta\underline{v}(P) \cdot 10^4$	$\Delta\underline{n}_D(V) \cdot 10^4$	$\Delta\underline{n}_C(V) \cdot 10^4$	$\Delta\underline{n}_F(V) \cdot 10^4$	$\Delta\Delta_{FC}^{20}$
0	0	0	1.6394	1.4384	1.4350	120.8	27.55	–	–	–	–	–
14.75	24.40	30.28	1.4439	1.4505	1.4467	141.9	31.50	+ 47	–32	–33	–23	+ 9.9
25.59	39.09	46.33	1.3300	1.4586	1.4545	150.6	32.84	+ 68	–43	–45	–33	+ 11.9
35.65	50.83	58.17	1.2406	1.4658	1.4616	156.7	33.63	+ 79	–45	–47	–34	+ 12.6
50.41	65.48	71.84	1.1309	1.4755	1.4711	162.9	34.26	+ 81	–40	–42	–30	+ 12.1
63.87	76.73	81.60	1.0479	1.4831	1.4786	165.7	34.30	+ 72	–34	–36	–26	+ 9.8
79.97	88.16	90.93	0.9645	1.4916	1.4870	167.1	33.99	+ 46	–21	–22	–16	+ 5.9
100	100	100	0.8788	1.5011	1.4965	166.6	33.25	–	–	–	–	–

The refractive index isotherms n_D^{20}, n_C^{20} and n_F^{20} are convex toward the axis of composition (in volumetric portions). The deviations from additivity $\Delta n(V)$ reach −0.0047, regularly decreasing from the red line C to the blue F line (Fig. 6). The negative values $\Delta n(V)$ are customary for normal or associated components, but they are not encountered in typical irrational systems [16].

It is of interest that the isotherms of refractive dispersion have another direction of curvature than n(V). The average dispersion $\Delta_{FC}^{20} = (n_F^{20} - n_C^{20}) \cdot 10^4$ displays a considerable positive deviation from additivity ($\Delta\Delta_{FC}^{20}$) as a function of the volumetric proportions. The values $\Delta\Delta_{FC}^{20}$ reach + 12.6 (Fig. 6). Such a great positive deviation of the average dispersion from additivity in solutions is a rather rare phenomenon.

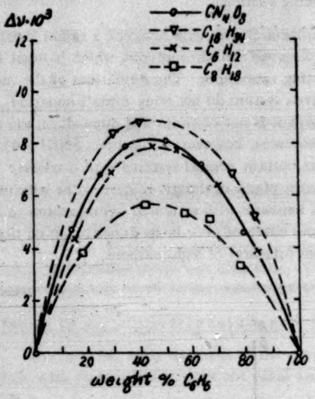

Fig. 5. Expansion in mixtures of benzene with tetranitromethane, cyclohexane [15], isooctane [14] and hexadecane [14].

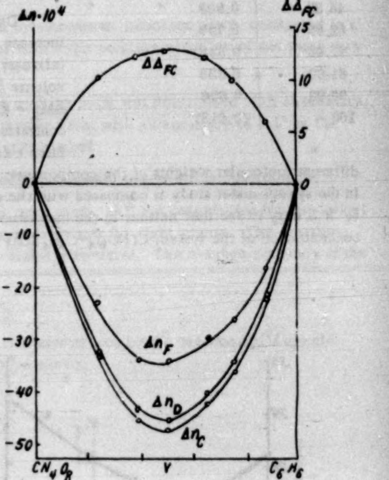

Fig. 6. Deviations from additivity of the indices of refraction and average dispersion.

The dispersive power $\omega_{FCD} = \frac{n_F - n_C}{n_D - 1} 10^3$ in the given system passes through a distinct maximum (Table 3). This, so far as is known, is the first case of a maximum ω_{FCD} in liquid systems.

The indicated peculiarities of refractive dispersion are doubtless associated with sharp changes in the absorption spectra in mixtures of tetranitromethane and benzene.

The results of the spectrophotometric investigations are presented in Fig. 7. On the curves of optical density − composition in the wave length range (422-458 mμ) studied, there are pronounced maxima at contents of benzene of 72-77 mol. %. Since tetranitromethane and benzene practically do not absorb in this region of the spectrum, the absorption which is observed in the mixtures must occur as the result of reaction of the components. There are no definite indications in the literature concerning the origin of the absorption band in mixtures of tetranitromethane with benzene. The coloration phenomenon is usually interpreted as a consequence of the formation of a compound of the components. We consider such an explanation entirely probable in the given case, since very considerable changes occur in the spectrum.

The distance between the short-wave boundary of the absorption band of tetranitromethane and the most intense coloration of its mixtures with benzene amounts to about 100-110 mμ according to our data (Fig. 8). A distance of about the same order of magnitude (∼ 180 mμ) exists between the maximum absorption of the vapors of tetranitromethane [6] and of a solution of its mixture with benzene in carbon tetrachloride [1]. In spite of the approximate evaluation of the positions of the absorption bands, it can be concluded that significant energetic changes in the component molecules, associated with changes in their structure, occur in the system.

During dilution of mixtures of tetranitromethane and benzene with carbon tetrachloride, the optical density rapidly falls, and does not obey the Lambert-Beer law, and the position of the maximum on the D – N curves is changed, approaching a molar component ratio of 1:1.

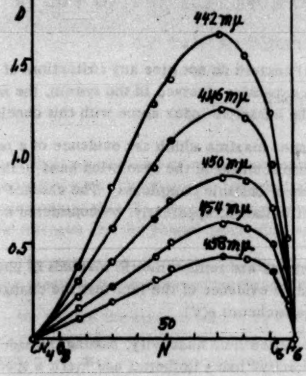

Fig. 7. Optical density (D), as a function of the composition of mixtures of tetranitromethane and benzene (in mol.%.

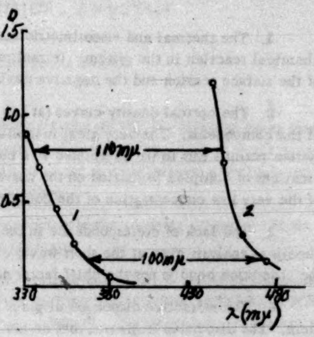

Fig. 8. Short-wave boundary of the absorption band of tetranitromethane (1) and mixtures of 72 mol.% $C(NO_2)_4$ + 28 mol % C_6H_6 (2).

The spectrophotometric measurements thus render very probable the hypothesis concerning the formation in the system: tetranitromethane – benzene of compounds of the components which are decomposed during dilution with a third component.

It is very interesting that the hypothetical compounds did not appear on one of the other property – composition diagrams studied by us. This fact, in all probability, is to be explained by the extraordinary instability of the complexes being formed and their very low concentrations in the system.

Hammick and co-workers [1] evaluated the concentration of the complex as being of the order of 10^{-4} moles/liter (in molar solution) on the basis of spectrophotometric study of solutions of $C(NO_2)_4$ and benzene in CCl_4. It is natural that admixture of such a small quantity of compound would not be appreciably reflected on the isotherms of many of the properties of the system.

The great sensitivity of the spectrophotometric method in the given case should by no means be interpreted in the sense either of its universality or of an exclusive position for it among other physico-chemical analytical methods. There is nc doubt that a profound and complete representation of the behavior of the components in solutions can be obtained only by complex investigation by various methods. However, for this purpose it is impossible to limit oneself to the traditional comparison of the form of the property–composition curves with the empirically established types of the isotherms and their classifications. Such a purely phenomenological method without knowledge of the quantitative laws determining the forms of the isotherms of each property can readily lead to erroneous conclusions, even if certain properties of the system are investigated.

In this connection the spectrophotometric and refractrometric data in the system under study were compared. It would appear that the close physical relation between the phenomena of absorption and refraction of light would have permitted one to expect a correspondence in the results of these methods; however, the formally described interpretation of the form of the refractive index isotherm leads to results directly opposed to the spectrum data. The curves $\underline{n}_\lambda - V$, convex toward the composition axis, become less curved in proportion as they approach the violet end of the spectrum and approach the straight line form of the isotherm of an ideal system. Thus, the deviations fom additivity which are considered in physico-chemical analysis as a criterion of an ideal system, in the given case diminish exactly in proportion as one approaches the region of the spectrum where reaction of the components appears particularly distinct (see Figs. 6 and 7). The explanation of this can only be given on the basis of the quantitative study of the various factors which influence the form of the isotherm $\underline{n}(V)$, to which it is proposed to devote a special investigation. It is evident from the example set forth that the position of the absorption band can not be considered a prime factor determining the form of the isotherm $\underline{n}$ (V). Volume changes occurring in the system exert a much stronger influence on it. In mixtures of $C(NO_2)_4$ with C_6H_6 the signs of $\Delta\underline{n}(V)$ and $\Delta\underline{v}(P)$ are usually found in agreement with the overwhelming majority of liquid systems [16, 17], in spite of the strong bathochromic displacement of the absorption band. This latter, acting in the direction opposed to the influence of expansion, only somewhat diminishes the absolute value of $\Delta\underline{n}(V)$, and does not change its sign.

SUMMARY

1. The thermal and viscosimetric methods of physico-chemical analysis do not give any indications of a chemical reaction in the system: tetranitromethane – benzene. The expansion observed in the system, the minimum of the surface tension and the negative deviation from additivity of the refractive index agree with this conclusion.

2. The optical density curves (at λ = 442-458mμ) have pronounced maxima which are evidence of a reaction of the components. The very great magnitude of the bathochromic displacement of the absorption band in the given system permits this to be interpreted as a consequence of the formation of unstable complexes. The absence of indications of complex formation on the curves of other physical properties should, apparently, be considered a result of the very low concentration of the complexes.

3. The lack of correspondence in the data of the spectrophotometric and refractometric methods of physico-chemical analysis even at the short-waves close to the absorption band, is evidence of the fact that the change in the absorption band is not the chief factor determining the form of the isotherms $\underline{n}(V)$.

4. The refractive dispersion displays a considerable positive deviation from additivity, passing through a maximum. The dispersion isotherms thus do not repeat the form of the refractive index isotherms and merit a special study.

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STUDY OF THE REACTION OF 8-HYDROXYQUINOLINE WITH ORGANIC ACIDS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

D. I. Dionisyev and Z. K. Dzhelomanova

8-Hydroxyquinoline or oxine, synthesized for the first time in 1859 by Lyubavin [1], has attained great importance in analytical chemistry for the qualitative and quantitative separation of metals, with which it forms strong complex compounds [2]. Its chemical properties are of interest on account of the mutual influence of the heterocyclic nitrogen and the phenol group which are in the o-position to each other.

The separation of metals with the aid of 8-hydroxyquinoline is conducted in the presence of organic acids, but the reaction of 8-hydroxyquinoline with these acids has not been investigated.

We studied the systems formed by 8-hydroxyquinoline with acetic, benzoic and salicylic acids by the melting point, viscosity, density and electrical conductivity methods and with the melting point method, additionally studied the systems formed by 8-hydroxyquinoline with monochloroacetic, p-hydroxybenzoic, p-nitrobenzoic, cinnamic and hydrocinnamic acids.

The method of investigation was the same as in the preceding works [3]. The viscosity was expressed in centipoises, the concentration – in mole per cent.

The System 8-Hydroxyquinoline – Acetic Acid

Glacial acetic acid after repeated fractional crystallization and boiling with acetic anhydride was carefully purified and had a m.p. of 16.5°, a b.p. of 118°, d_4^{60} 1.0105. "Pure" brand 8-hydroxyquinoline was recrystallized several times from ethyl alcohol, m.p. 75°, d_4^{80} 1.1594.

The results of the melting point measurements are presented on Fig. 1.

The melting point curve consists of two branches. We did not succeed in producing crystallization in the section from 25 to 10 mole %. There is a maximum on the viscosity isotherm η (Fig. 2) corresponding to 35 mole % of 8-hydroxyquinoline which partially explains the formation of glasses in the solid phase. The viscosity isotherm is convex toward the composition axis in the section from 100 to 60 mole %, which is evidence of the decomposition of acetic acid dimers. There is a maximum on the curve of the temperature coefficient of viscosity γ which corresponds to 35 mole % of 8-hydroxyquinoline. This is evidence of the fact that a compound with a component ratio 1: 2 of the composition $C_9H_7NO \cdot 2CH_3COOH$ is formed in the liquid phase. There are pronounced maxima on the electrical conductivity isotherms κ (Fig. 3) which correspond

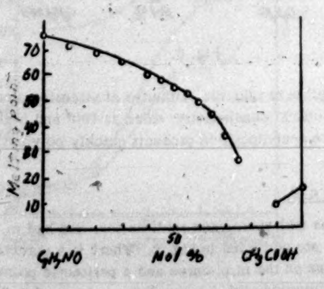

Fig. 1.

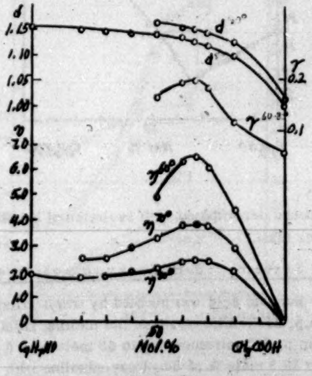

Fig. 2.

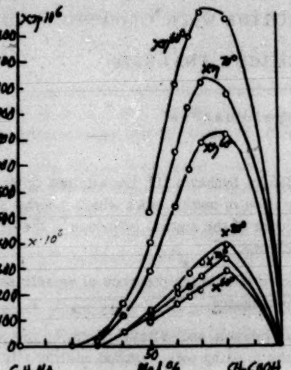

Fig. 3.

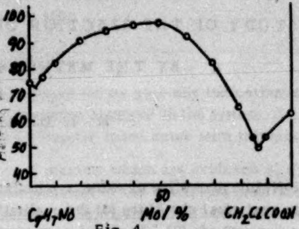

Fig. 4.

to 20 mole % of 8-hydroxyquinoline. By correcting the electrical conductivity for the viscosity $\kappa\eta$ the maxima on the curves are displaced by approximately 30 mole % of 8-hydroxyquinoline, which also confirms the formation of a compound $C_9H_7NO \cdot 2CH_3COOH$ in the liquid phase.

The System: 8-Hydroxyquinoline – Monochloroacetic Acid

Monochloroacetic acid was purified by distillation and was kept in sealed ampoules. It had m.p. 63° and b.p. 186.5°.

The results of the freezing point measurements of the given system are portrayed in Fig. 4. During the reaction of monochloroacetic acid with 8-hydroxyquinoline a compound is formed with a ratio of components of 1:1 of the composition $C_9H_7NO \cdot CH_2ClCOOH$, which corresponds to a maximum on the freezing point curve at 50 mole % of 8-hydroxyquinoline and m.p. of 98°, and also eutectic points. The first eutectic point with m.p. 73° corresponds to 89 mole % of 8-hydroxyquinoline, the second eutectic point with m.p. 49° corresponds to 30 mole % of 8-hydroxyquinoline. The maximum is diffuse which is evidence of dissociation of the compound during fusion. It was not possible to take the isotherms of viscosity, density and electrical conductivity, since at 100° and higher the compound decomposed with evolution of bubbles of gas, and the decomposition products quickly polymerized into a thick mass.

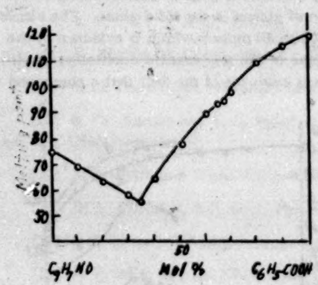

Fig. 5.

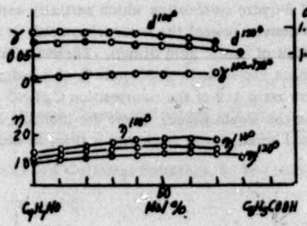

Fig. 6.

The System: 8-Hydroxyquinoline – Benzoic Acid

Benzoic acid was purified by recrystallization from water with subsequent sublimation, and had m.p. 121.7° and b.p. 249°. The results of the melting point measurements are portrayed in Fig. 5. There is a eutectic point with m.p. 56° corresponding to 65 mole % of 8-hydroxyquinoline on the m.p. curve and a peritectic point corresponding to 33.3 mole % of 8-hydroxyquinoline with m.p. 95°. A compound with a ratio of components of 1:2 of the composition $C_9H_7NO \cdot 2C_6H_5COOH$ is evidently formed in the liquid phase and the peritectic point coincides with

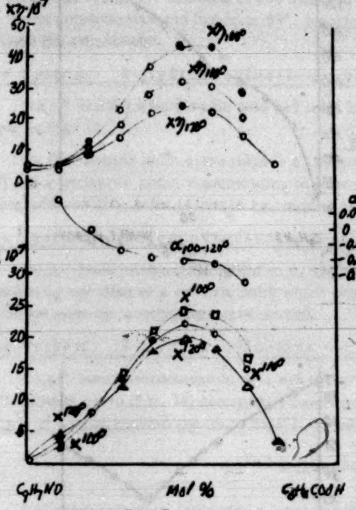

Fig. 7.

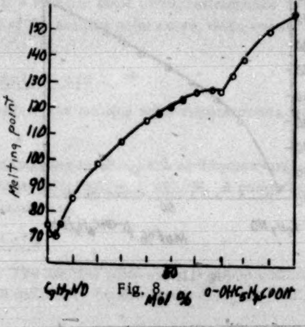

Fig. 8

the maximum corresponding to the compound set forth above. We did not succeed in taking a cooling curve in view of the strong supercooling of the mixtures.

The viscosity isotherms (Fig. 6) are strongly flattened toward the composition axis; they have very diffuse maxima which correspond to 40 mole % of 8-hydroxyquinoline. There are no singular points on the curve of the temperature coefficient of viscosity γ (100-120°). The electrical conductivity isotherms consist of curves with a maximum corresponding to 50 mole % of 8-hydroxyquinoline (Fig. 7). Correcting the electrical conductivity for viscosity displaces the maximum on the curves to values of from 40 mole % of 8-hydroxyquinoline at 100° to 50 mole % of 8-hydroxyquinoline at 120°. The curve of the temperature coefficient of electrical conductivity α has an inflection point corresponding to 50 mole % of 8-hydroxyquinoline. On the section of the curve for from 80 to 20 mole % of 8-hydroxyquinoline the values of the temperature coefficient of electrical conductivity have a negative sign.

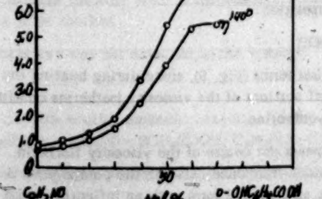

Fig. 9.

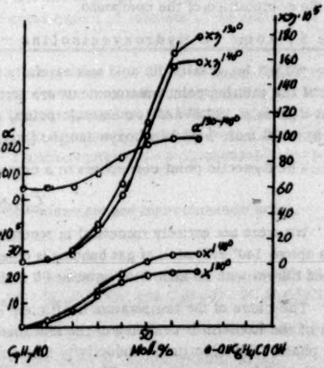

Fig. 10.

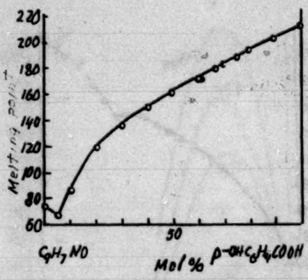

Fig. 11.

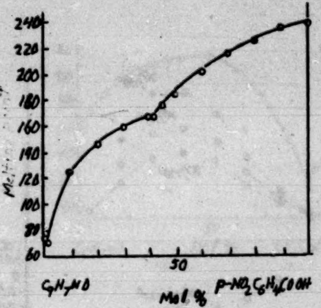

Fig. 12.

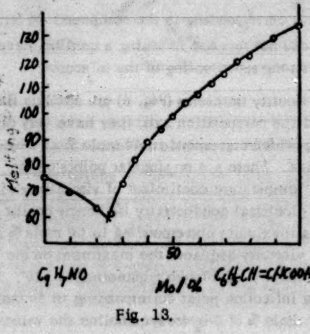

Fig. 13.

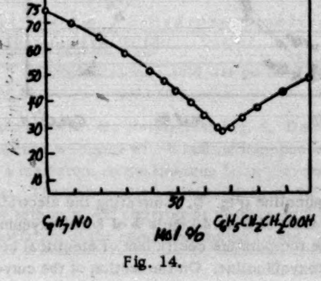

Fig. 14.

On the basis of the data obtained it can be assumed that a compound exists in the liquid phase, but in view of the low values of the magnitudes of the electrical conductivity, it is impossible to say anything definite concerning the composition of the compound.

The System: 8-Hydroxyquinoline – Salicylic Acid

"C.p." brand salicylic acid was carefully purified by repeated recrystallization and had m.p. 156°. The results of the melting point measurements are portrayed in Fig. 8. On the melting point curve there is a dystectic point with m.p. 127.5° and two eutectic points, which correspond 1) to 97 mole % of 8-hydroxyquinoline (m.p. 70°), and 2) to 29 mole % of 8-hydroxyquinoline (m.p. 126°).

The dystectic point corresponds to a compound of the composition

$$C_9H_7NO \cdot 2C_6H_4OHCOOH,$$

We were not entirely successful in recording the viscosity isotherms (Fig. 9), since during heating the mixtures above 140° evolution of gas bubbles is observed. The cut-off portions of the viscosity isotherms consist of S-shaped curves with an inflection point at 60 mole % of 8-hydroxyquinoline.

The curve of the temperature coefficient of viscosity γ ~~repeats the~~ course of the viscosity isotherm. The form of the isotherm is evidence of the fact that there is a chemical compound between the components in the liquid phase. The electrical conductivity isotherms (Fig. 10) have an S-shaped form with an inflection point at 80 mole % of 8-hydroxyquinoline. The character of the curves is not changed by correcting the electrical conductivity for viscosity.

The System: 8-Hydroxyquinoline – p-Hydroxybenzoic Acid

p-Hydroxybenzoic acid was purified by recrystallization from ethyl alcohol and had m.p. 219°. The melting point curve (Fig. 11) consisted of two branches intersecting in a eutectic point which corresponded to 6 mole % of 8-hydroxyquinoline and had m.p. 67°. Judging by the form of the melting point curve, there was no reaction between the components.

The System: 8-Hydroxyquinoline – p-Nitrobenzoic Acid

"C.p." brand p-nitrobenzoic acid had m.p. 238°. The results of the melting point measurements are portrayed in Fig. 12.

On the melting point curve there is a eutectic point corresponding to 99 mole % of 8-hydroxyquinoline (m.p. 72°) and a peritectic point, corresponding to 58 mole % of 8-hydroxyquinoline (m.p. 168.5°). A compound with an incongruent melting point is formed by reaction between the components.

The System: 8-Hydroxyquinoline – Cinnamic Acid

"C.p." brand cinnamic acid had m.p. 134° and b.p. 300°. The melting point curve (Fig. 13) consisted of two branches intersecting at a eutectic point which corresponds to 70 mole % of 8-hydroxyquinoline (m.p. 60°). No reaction between the components was detected.

The System: 8-Hydroxyquinoline – Hydrocinnamic Acid

"C.p." brand hydrocinnamic acid was recrystallized from alcohol and had m.p. 49° and b.p. 279.5°. The melting point curve (Fig. 14) consisted of two branches intersecting in a eutectic point which corresponded to 32 mole % of 8-hydroxyquinoline (m.p. 28.5°). There was no reaction between the components.

DISCUSSION OF RESULTS

8-Hydroxyquinoline containing a heterocyclic nitrogen atom and a hydroxyl group, can, depending on the nature of the substance reacting with it, assume either a basic or an acidic character. When reacting with a substance of an acidic character, the 8-hydroxyquinoline displays basic properties. Thus, by reaction of 8-hydroxyquinoline with acetic acid a compound of the composition 1:2 (two molecules of acid) is formed.

During the addition of acetic acid to 8-hydroxyquinoline, decomposition of its dimers occurs and is reflected in the viscosity isotherms; it is the monomers of acetic acid which react with the 8-hydroxyquinoline.

The activity of acetic acid is increased by the introduction of chlorine into the molecule. A compound of the composition 1:1 detected by the melting point method in the given system was possibly formed in an acid-base reaction. In the system: 8-hydroxyquinoline – hydroxybenzoic acid, as well as in the system with acetic acid, a compound of the composition 1:2 was detected. The introduction into the molecule of benzoic acid of a hydroxyl group in the ortho position, increases its acidic properties, and one could expect an increase in the activity of the reaction of 8-hydroxyquinoline with salicyclic acid.

Actually, a compound with a congruent melting point with a composition of 1:2 was detected in this system by the melting point method. But chemical reaction between the components was not detected during the introduction of a hydroxyl group into benzoic acid. If one introduces the nitrogroup into the benzoic acid molecule in the para-position, then its activity with respect to 8-hydroxyquinoline is partially increased, and a compound with an incongruent melting point is successfully shown in the system: 8-hydroxyquinoline – p-nitrobenzoic acid by the melting point method.

Reaction was not detected in the systems: 8-hydroxyquinoline – cinnamic and hydrocinnamic acids.

SUMMARY

1. With acetic, monochloroacetic, benzoic and salicylic acids 8-hydroxyquinoline forms compounds of the composition: $C_9H_7NO \cdot 2CH_3COOH$, $C_9H_7NO \cdot CH_2ClCOOH$, $C_9H_7NO \cdot 2C_6H_5COOH$ and $C_9H_7NO \cdot 2C_6H_4OHCOOH$.

2. 8-Hydroxyquinoline forms a compound with an incongruent melting point with p-nitrobenzoic acid.

3. 8-Hydroxyquinoline does not react with p-hydroxybenzoic, cinnamic or hydrocinnamic acids.

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* See Consultants Bureau Translation, page 2143.

ALKYLATION OF AROMATIC HYDROCARBONS WITH OLEFINS

IN THE PRESENCE OF METALLIC ALUMINUM AND HALOGEN DERIVATIVES

N. G. Sidorova, I. P. Tsukervanik and E. Pak

In a preceding communication [1], the condensation reaction of halogen derivatives with aromatic hydrocarbons in the presence of metallic aluminum pioneered by Radziwanowski [2] and later studied by Azatyan [3], was studied by us. We accomplished the condensation of a number of chlorine (and partially of bromine) alkyls with benzene and toluene. We obtained the following yields of monoalkylated hydrocarbons by this route: ethylbenzene 74%; sec.-butylbenzene 81%; sec.-butyltoluene 64%; isoamylbenzene 60%; sec.-octylbenzene 47%; and diphenylmethane 70% of the theoretical. This method of synthesis is simpler and better for diphenylmethane than that known in the literature [4].

This method of preparing alkylbenzenes has great advantages as compared with the classical synthesis of Gustavson—Friedel—Crafts. It was natural to attempt to extend it to the alkylation of aromatic hydrocarbons with olefins. During the alkylation of halogen derivatives,they initially form halogen aluminates with metallic aluminum,which subsequently induce condensation of alkyl halides with aromatic hydrocarbons. The addition of some extraneous substance capable of yielding $AlCl_3$ or $AlBr_3$ with metallic aluminum was necessary for alkylation with olefins. Either hydrogen chloride, employed for the first time by Radziwanowski [2] in the condensation reactions of halogen derivatives with aromatic hydrocarbons in the presence of aluminum or bromine recently utilized in such syntheses [5] could serve as such additions. Such catalysts have not been employed by anyone for the alkylation of olefins.

We employed halogen derivatives as additives. The role of the halogen derivatives was twofold in this case: they serve for the preparation of $AlCl_3$ and are alkylating substances. Such a variation in the alkylation is even more efficient than the condensation of alkyl halides with aromatic hydrocarbons in the presence of metallic aluminum. Here we replace the greater part of the expensive halogen derivatives with the cheap olefins.

We studied the alkylation of benzene by ethylene, propylene, isobutylene, isoamylene and cyclohexene. As addition agent we used (mostly) the alkyl halide (chiefly the chloride) corresponding to the olefins. The quantity of aluminum employed does not have great significance, since only a small part of it enters into the reaction.

All the reactions gave a positive result. The yields of monoalkylated hydrocarbons amounted to 40-71% of the theoretical calculating on the basis of the olefin entering into the reaction and the alkyl halide taken. The reaction proceeds very well with the low molecular weight olefins at room temperature, but with increase in the molecular weight of the olefin a higher temperature is required. We noted in addition that the bulk of the olefin did not react during very energetic stirring. We therefore conducted all the subsequent experiments with moderate stirring and slow passage of the olefin. More complete absorption of the olefin proceeded in this case.

EXPERIMENTAL

The metallic aluminum necessary for the reaction was rapidly rubbed with a file into the form of a coarse powder and immediately drenched with benzene to protect it from oxidation by atmospheric oxygen.

All the olefins used in the condensations were prepared by dehydrogenation of alcohols over aluminum oxide.

The reactions were conducted in a three-necked flask with a reflux condenser, a thermometer and a tube for supplying the olefin. The gaseous olefins were admitted into the reaction from a gas holder after having been preliminarily conducted through a tall calcium chloride column. In the case of isoamylene and cyclohexene, in place of this tube, a dropping funnel was substituted, by the aid of which a solution of the olefin in an aromatic hydrocarbon was added. The end of the condenser was joined, through a calcium chloride tube and a Tishchenko bottle, with a second gas holder to collect the unreacted olefin. It was necessary to clean the apparatus carefully, since otherwise the reaction could either not proceed or could only begin after prolonged heating of the mixture.

The order of conducting the condensations was the same in all the experiments. The mixture of benzene, halogen derivative and metallic aluminum was heated at the boiling temperature until the reaction began, which was noted by the evolution of hydrogen chloride and darkening of the mixture. After this the needed temperature was established and the olefin was released at such a rate that the bubbles could be counted. The mixture was then usually left to stand until the following day, after which decomposition with water and acidification with hydrochloric acid was carried out. The hydrocarbon layer was separated, washed with water, dried over calcium chloride and fractionated. The hydrocarbons obtained were again redistilled over sodium. The excess benzene was used again after purification.

The condensations which gave the best results are summarized in Table 1. The physical properties of the hydrocarbons prepared are summarized in Table 2.

TABLE 1

Results of the Condensation of Olefins with Benzene

Starting materials				Temperature (in °)	Yield of products	
Olefin (in liters)	Benzene (in g)	Halogen derivative (in g)	Aluminum (in g)		Monoalkylated (in g)	Di- and polyalkylated (g)
Ethylene 2.0	120	n-C_4H_9Cl 13.3	0.1	20-30	4.2 (47.7%)	1
Propylene 3.0	100	iso-C_3H_7Br 3.5	0.15	20-23	13.0 (71%)	2.5
Isobutylene 4.0	100	n-C_4H_9Cl 3.7	0.2	40-45	10.7 (40%)	8
Isoamylene 8.2 g . . .	50	iso-$C_5H_{11}Cl$ 1.85	0.2	75-80	9.0 (45.5%)	0.9
Cyclohexene 8.2 g . .	60	n-C_4H_9Cl 1.0	0.1	60	7.0 (41%)	3.0

TABLE 2

Physical Properties of the Hydrocarbons

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}	Found MR_D	Calculated MR_D
Ethylbenzene	134° (725 mm)	0.8664	1.4957	35.75	35.55
Isopropylbenzene	150-150.5 (725 mm)	0.8630	1.4899	40.19	40.17
tert.-Butylbenzene	165-166 (725 mm)	0.8670	1.4907	44.78	44.79
tert.-Amylbenzene	186-187 (725 mm)	0.8648	1.4904	49.56	49.41
Phenylcyclohexane	233-235 (722 mm)	0.9428	1.5228	51.87	51.82

SUMMARY

The possibility was demonstrated of alkylating aromatic hydrocarbons with olefins in the presence of metallic aluminum with the addition of halogen derivatives. The yield of monoalkylated hydrocarbons amounted to 40-71% of the theoretical.

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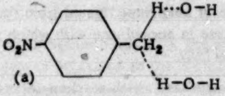
INVESTIGATION OF THE MIGRATION ROUTES OF THE HYDROGEN ATOM DURING CERTAIN OXIDATION-REDUCTION REACTIONS. I

A. F. Rekasheva and G. P. Miklukhin

The covalent bond can be cleaved either with the formation of two neutral radicals, each of which retains one electron of the bond pair, or with the formation of two ions, one of which retains both electrons. The first type of bond cleavage is called homolytic or radical; the second – heterolytic or ionic [1].

Homolysis of bonds is energetically more efficient for any given molecule than heterolysis, since during the latter process it is necessary to expend additional energy to separate the charged ions. For this reason the majority of gaseous reactions are of the atomic or homolytic type. In solutions, however, it is necessary to take into account the electrostatic reaction of the molecules of the reacting substances with the solvent, which not only lowers the electrostatic work of separating the ions in the moment of the reaction, but also extends the polar bond prior to the act of reaction of either compound. It is precisely on this account that the majority of reactions in solutions have an ionic mechanism, i.e., proceed with heterolysis of the bonds.

Specification of an ionic cleavage mechanism does not mean an obligatory formation of free ions in solution. We can refer to the exchange reaction between 2-nitrotoluene and heavy water [2] as an example. This process certainly has an ionic mechanism; we do not, however, suppose that ions of 2-nitrotoluene actually exist in solution. In all probability, the reaction proceeds due to the formation of complexes between water, nitrotoluene and a catalyzing base, for example (a).



(a)

Exactly such a process was proposed in the works of A. I. Shatenshtein and coworkers [3] who were studying the exchange reactions of hydrocarbons with liquid deuterio-ammonia.

We consider the actual formation of free radicals as entirely non-obligatory, just as in the case of the homolytic cleavage of bonds. In what follows we shall speak of the radical or ionic cleavage of bonds, of their homolysis and heterolysis, without linking these phenomena with the question of the presence of free radicals or ions in the reaction mixtures.

It has long been known that the method of labeled atoms, along with the kinetic, spectrum and others, is one of the most important methods for the study of the mechanisms of chemical reactions [4-7]. There is, moreover, a whole series of questions for the resolution of which this method is unique. In particular, only with the aid of the labeled atom method can the route of migration of various atoms of either compound in various reactions be established without any reliance on analogy.

It is precisely this latter question concerning the routes of migration of atoms in reactions to which the several investigations, the results of which are summarized in this communication, are dedicated.

It is necessary to underline here the basic premises of this series of our works. In all probability, the question of bond strength should play a subordinate role in the consideration of ionic processes. Hydrogen entering into the composition of compounds in bonds such as that with oxygen exchanges very rapidly, while in bonds with carbon the exchange of hydrogen atoms proceeds, on the contrary, very slowly. At the same time, the O – H bond is considerably stronger than the C – H bond. Consequently, in ionic exchanges and, in all probability, in all other reactions, it is not the strength of the bonds that determines the direction of the reaction. As was demonstrated by Brodsky [8] and confirmed in his works with Sulima and Khaskina [9, 10], exchange reactions proceed rapidly under conditions in which the atoms linked with the exchanging hydrogen have free electron pairs (nitrogen in NH_3, oxygen in H_2O, etc.). We have already expressed the hypothesis in other works that ionic reactions are realized, in all probability, at the expense of cleavage of the most polar bonds [29].

During homolytic processes* the situation should be reversed: the polar bonds play no role; the course of the reaction is determined by the strength of the bonds. If this basic position is correct, then in a case when compounds containing hydrogen in O – H and C – H bonds are present in the reaction mixture, the hydrogen of the C – H bonds, as the least strong, should react in homolytic processes. This assumption could only be demonstrated with the aid of an isotopic method which permitted the substitution of the hydrogen of the O – H, C – H and other bonds and the elucidation of the routes of its migration during the reactions.**

Prior to our works several processes in which migration of the usually non-labile hydrogen atoms of the C – H bonds occurred had already been studied. Thus, during the Canizzaro reaction [11] the formation of alcohol was established by way of the direct migration of hydrogen from the C – H bond of one molecule of aldehyde to the C – H bond of another. During the electrolysis of salts of fatty acids, the radicals being formed during the disproportionation, transfer hydrogen atoms directly to each other without the participation of other molecules [12]. The methane evolved during the electrolysis of heavy acetic acid CD_3COOH in ordinary water has a composition CD_4, i.e., the methyl radical CD_3 formed from the acid, captures deuterium from other acid molecules, but not hydrogen from the solvent [13]. Further, during the reaction of formaldehyde with hydrogen peroxide in heavy water light water is evolved, which is evidence of the direct joining of two hydrogen atoms originating from two formaldehyde molecules [14]. It has recently been demonstrated that a similar homolytic process takes place also during the decomposition of the peroxides of organic acids [15]. Finally, G. A. Razuvaev, G. G. Petukhov and the authors [16] have demonstrated that during the photoreaction of phenylmercury hydroxide with methyl or ethyl alcohols containing deuterium in the hydroxyl group, light benzene is formed, which is evidence of the capture by the phenyl residue of ordinary water from the C – H bonds of the alcohol, and not deuterium from its O – H bond.

We selected the reduction reaction of diazonium salts and aldehydes as the subject of the investigation, since there are indications suggesting that these processes are probably of a homolytic character [1, 17].

Reduction of Diazonium Salts with Ethyl Alcohol

The reduction of diazonium salts by ethyl alcohol is one of the most studied and widely applied methods of removing the amino group [18]. We studied the deamination reaction with ethyl alcohol containing deuterium in the hydroxyl group.*** The object of the work was to establish the source of the hydrogen which is transferred to the hydrocarbon from the alcohol. It is evident that both the hydrogen of the O – H bond of the alcohol, and the hydrogen of its C – H bond can participate in the reaction. The mechanism of the reaction of deamination with alcohols has never been investigated from this point of view. Until very recently, hypotheses have been advanced in the literature in accordance with which the hydrogen atoms migrate to the hydrocarbon from the O – H groups of the alcohol [20].

Dry p-nitro- and m-chlorophenyldiazonium chlorides were prepared by the diazotization of the hydrochlorides of the corresponding amines with isobutylnitrite in absolute alcohol. After precipitation and washing the diazonium salts with absolute ether, they were quickly pressed out on filter paper and placed in absolute ethyl alcohol containing deuterium in the hydroxyl group and cooled to 0°. The latter was prepared by addition of deuterium oxide to absolute ethyl alcohol. After 24 hours a calculated quantity of metallic sodium (10% excess) was added to the alcohol, and the mixture, protected from moisture with a calcium chloride tube, was fractionated with a good fractionating column. The heavy ethyl alcohol was collected within limits of 0.3°.

The mixture of dry diazonium salts with heavy ethyl alcohol was very slowly heated to the boiling point in a flask supplied with a condenser and a calcium chloride tube. A very violent reaction course was observed in several experiments, with ejection of a portion of the reaction mixture through the condenser. After completion of the reaction the basic mass of the alcohol was slowly distilled off, and the benzene derivatives were separated from the residue by steam distillation, dried and fractionated. Nitrobenzene was collected within the range of 209-211°, chlorobenzene boiled at 129-131° (756 mm).

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* We denote a process homolytic or heterolytic if the stage of the reaction of interest to us – the migration of hydrogen – proceeds respectively with homolysis or heterolysis.

** The complete absence of substantiated experimental data concerning the role of the hydride ions H^- in reactions of organic compounds permits us to ignore mechanisms involving them with reference to the processes under study.

*** A brief communication concerning this investigation was published earlier [19].

The alcohol was purified by repeated distillation, finally over calcium oxide and with the addition of metallic sodium. The fraction was collected which had b.p. 78-78.5°, n_D^{22} 1.3608-1.3615.

The purified benzene derivatives and the alcohol were burned over cupric oxide in a stream of dry air, and the water from the combustion was analyzed for its dueterium content by the flotation method. In contrast with the procedure ordinarily employed [18], with the object of economizing deuterium, we did not use a large excess of alcohol (30-40 ml of heavy ethyl alcohol for the quantity of diazonium salt obtained from 0.1 mole of the starting amine were taken for the reaction). In connection with this, the yields of benzene derivatives were small: they amounted to 30-40% for nitrobenzene, and 25-35% for chlorobenzene, calculated in each case on the basis of the amount of amine.

The deamination of 3-nitro-4-aminotoluene was conducted in a water-alcohol solution [21]. A solution of 16 g of amine in 50-70 ml of ordinary alcohol was mixed with 24 g of concentrated sulfuric acid (Sp. gr. 1.83) and diazotized with a solution of 8.2 g of sodium nitrite in 10 ml of deuterium oxide (6000γ). The alcohol was distilled off with a fractionating column and purified as described above. 3-Nitrotoluene was isolated from the residue after distilling off the alcohol by steam distillation. The purified dry benzene derivative and the alcohol were burned, and the density of the water of combustion was determined by the usual method. The results of the experiments are summarized in Table 1.

TABLE 1

Benzene derivative obtained	Deuterium content (in γ)			
	in the water from the combustion of ethyl alcohol	in the hydroxyl group of the ethyl alcohol	in the water from the combustion of the benzene derivative	
			Found	Calculated
Nitrobenzene	410	2460	21	490
	445	2670	9	535
	440	2640	26	530
	–	–	11	–
Chlorobenzene	380	2280	24	455
	370	2220	11	445
3-Nitrotoluene	560	3360	17	480
	630	3780	5	540

During the combustion of the organic compound (over cupric oxide in a stream of dry air), the deuterium present in some position of the molecule, is diluted by the rest of the hydrogen contained in the molecule. Knowing the deuterium content in the water from the combustion of the alcohol, one can readily calculate its content in the hydroxyl group of the alcohol prior to combustion: it is 6 times greater, since the ethyl alcohol molecule contains 6 hydrogen atoms. These quantities are set forth in the third column of Table 1.

If the diazo group of the diazonium salts had been substituted during the reduction by the hydrogen of the hydroxyl group of the alcohol, then the deuterium content in that position of the benzene derivative which was previously occupied by the diazo group should have corresponded to the deuterium content of the hydroxyl group of the ethyl alcohol. The quantity of deuterium in the water of combustion of the given benzene derivative would be as many times less as the deuterium is diluted by hydrogen during the combustion. If there are m hydrogen atoms in the molecule of the benzene derivative, and the content of deuterium in the hydroxyl group of the ethyl alcohol amounts to A, then the content of deuterium in the water from the combustion of the hydrocarbon should be equal to A/m, if the hydrogen of the OH group of the alcohol participates in its formation. The numbers obtained by such a calculation are set forth in the last column of Table 1. Comparison of these quantities with those found experimentally convinces one of the fact that during the reduction of the diazonium salts by ethyl alcohol, hydrogen atoms are transferred to the benzene derivative being formed not from the OH group but from the CH bonds of the reducing agent. The small amount of heavy water in the water of combustion is to be explained both by contamination of the hydrocarbons with small quantities of organic compounds capable of exchanging their hydrogen atoms with the deuterium of the alcohol under the conditions of the experiments (for example, phenyl ethers [22]), and by the difficulty of purifying the analyzed samples of water from the last traces of foreign substances. The errors in measurement amount to 10-15γ, ordinarily in the direction of overstatement.

Thus, the benzene derivatives isolated by us practically do not contain deuterium. Consequently, hydrogen atoms of the CH bonds of the alcohol participate in the formation of benzene derivatives during the reduction of diazonium salts with ethyl alcohol. Taking into account that the diazonium salts are reduced by such alcohols as benzyl, it can be assumed that the hydrogen is in all cases cleaved from the α-carbon atom of the alcohols, and, consequently, the reduction reaction can be portrayed by the scheme:

$$RN_2Cl + CH_3CH_2OD \rightarrow RH + N_2 + DCl + CH_3CHO.$$

Investigation of the mechanism of a reaction by a single method very rarely can lead to the detailed solution of a problem. It is natural that in the given case a more detailed elucidation of the reaction mechanism of the deamination of diazonium salts by alcohols is not possible on the basis of the data obtained.

Reduction of Diazonium Salts by Hypophosphorous Acid

The deamination reaction was also studied by us using hypophosphorous acid as the reducing agent.* The possibility of reducing diazonium salts with hypcphosphorous acid was demonstrated 50 years ago [23], and this method of deamiaation has been widely disseminated since then [18].

However, with the exception of a few investigations of the last few years, parctically nothing has been done to elucidate the mechanism of this reaction. There exists indirect evidence that this reaction of diazonium salt reduction proceeds by a chain mechanism with the participation of free radicals [24]. The authors of that investigation assumed that during the reaction hydrocarbon radicals are joined with hydrogen atoms and bound with the hypophosphorous acid through the phosphorus and not through oxygen, but no evidence whatsoever for this assumption was adduced.

Resolution of the question of how the hydrogen atoms of the hypophosphorous acid transfer to the hydrocarbon during the reduction of its diazonium salts is complicated first of all by the fact that, as Brodsky and Sulima [25] showed, hypophosphorous acid comparatively rapidly exchanges hydrogen atoms of the P—H bonds with the deuterium of heavy water. A second difficulty consists of the fact that in the reaction under investigation, as in a number of others, the rates of exchange of hydrogen and deuterium are variable.

The experimental data obtained by us demonstrate that the exchange reaction between the hydrogen atoms of water and the hydrogen atoms of the P—H bonds of hypophosphorous acid proceeds more slowly than the reduction reaction, particularly if the latter is conducted in the presence of catalyst (cupric sulfate). In the latter case the deamination process is successfully completed for the basic mass of diazonium salt before a considerable quantity of hypophosphorous acid molecules with deuterium in the P—H bonds appears in the mixture.

We should dwell in somewhat greater detail on the question of the fact that the rates of transfer of hydrogen and of deuterium do not coincide. This phenomenon was long ago detected for certain reactions [27]. It depends on the fact that rupture of the bond: element—deuterium requires greater activation energy than the rupture of the corresponding bond: element—hydrogen. In reversible reactions, for example, during the ordinary exchange reactions of hydrogen isotopes [4, 5] or during the distribution of deuterium between light and heavy benzene in the presence of aluminum chloride [28], this difference in the equilibrium distribution of hydrogen and deuterium is not important, since toward the moment of reaching the equilibrium state, hydrogen and deuterium manage to be distributed equally between the participants in the process and migrate reversibly from one compound to the other. However, during irreversible processes, when the hydrogen and deuterium atoms can transfer only in one direction, a comparatively smaller quantity of that isotope which is more strongly bound to the molecule participates in the reaction. Its concentration in the reaction product will be lower than would be expected if analgous bonds of both isotopes were equivalent. In a given case—the reduction, for example, of p-toluyldiazonium chloride by hypophosphorous acid, there was shown to be 3-4 times less deuterium in the para-position of the toluene obtained than there was in the P—H bonds of the reducing acid.** Consequently, in the water from the combustion of this toluene, 24-32 times less deuterium is contained than in the P—H bonds of hypophosphorous acid. In connection with this, it was necessary to work at very high dilution with the starting compounds concentrated in deuterium, and all the relative errors of measurement were greater than usual.

We describe a typical reduction experiment. p-Toluidine (11 g) in an alcoholic solution was saturated with dry hydrogen chloride and diazotized with butyl nitrite. The crystalline diazonium salt precipitated with ether was filtered off, washed with ether and dissolved in water. An approximately 55% solution of hypophosphorous acid* was slowly added to the solution of diazonium salt at a temperature of −5 to +5°. After 24 hours the toluene formed was extracted from the reaction mixture with ether, washed with a solution of sodium hydroxide and then with water, dried with metallic sodium and fractionated. The toluene boiled over a range of 0.5°; n_D^{20} 1.4940-1.4957.** The purified toluene was burned over cupric oxide and the water from the combustion was analyzed for its deuterium content. The water from the reaction mixture after removing the toluene was distilled off in a vacuum and subjected to purification over incandescent cupric oxide, after which it was analyzed by the usual method. The results of the experiments are summarized in Table 2.

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*A brief communication was published previously [30].

**Similar magnitudes were obtained by Alexander and Burge [26]. We became aware of this work only after our basic experiments had been conducted.

The goal of the present work was the elucidation of the source of the hydrogen transferred to the hydrocarbon during the reduction of the diazonium salts by hypophosphorous acid. If the hydrogen atoms of the P−H bonds of the acid were not exchanged for heavy water deuterium atoms, the question would be resolved simply: during the reduction of ordinary hypophosphorous acid dissolved in heavy water, the hydrocarbon being formed from the diazonium salt would not contain deuterium if the hydrogen of the P−H bonds reacted, and would contain deuterium if the hydrogen were transferred to the residue of the diazonium salt from the H−O bond of the acid. We studied such a reaction in the case of the reduction of diazonium salts by ethyl alcohol, in which the hydrogen of the C−H bond is not exchanged for the heavy water deuterium. On the other hand, if the hydrogen of the P−H bonds of hypophosphorous acid were instantly exchanged with the heavy water deuterium, then the problem formulated above could not in general be resolved, since there would be no distinction between the hydrogen atoms bound in the acid. However, if an exchange reaction occurs, but proceeds somewhat more slowly than the reduction reaction, choice between the O−H and P−H bonds of the reducing agent becomes possible. If P−H bond hydrogen is transferred to the diazonium salt radical, then during the reduction of the diazonium salt dissolved in heavy water by ordinary hypophosphorous acid, there should be considerably less deuterium in the hydrocarbon than during the reduction of diazonium salt dissolved in ordinary water by heavy hypophosphorous acid containing deuterium in the P−H bonds. This is natural since in the first case, it would primarily be hydrogen of the P−H bonds of the light acid and in the second case, primarily deuterium bound to the phosphorous in the heavy acid, that would be transferred to the hydrocarbon radical.

To aid in drawing quantitative conclusions concerning the source of the hydrogen which is transferred to the hydrocarbon we introduced the concept of the "% transfer of deuterium". Let us assume that the hydrogen of the P−H bonds of hypophosphorous acid instantaneously exchanges with the deuterium of the heavy water. In such a case it is not difficult to calculate how much deuterium there will be in the hydrocarbon obtained during the reaction, independently of whether the reduction is effected by light or heavy acid. It is evident that in this case there should be as great a portion of deuterium in the hydrocarbon as in the reaction mixture for the entire period during which the process proceeds ($d_{av.}$, Table 2). As a result of the difference in the rates of transfer of hydrogen and of deuterium to the hydrocarbon, while isotopic equilibrium is being established in the exchange reaction, i.e., during the reduction of heavy acid in heavy water, less deuterium is transferred, approximately 32% of the calculated value (Experiment 9, Table 2). This quantity, called by us "% transfer of deuterium" (last column, Table 2) is determined by dividing the experimentally found content of deuterium in one position of the hydrocarbon (d_h) by the average deuterium content in the reaction mixture ($d_{av.}$). As is evident from the data summarized in Table 2, during the reduction of diazonium salt dissolved in heavy water by ordinary hypophosphorous acid (in the presence of cupric sulfate, Experiments 10-12), considerably less deuterium is found in the hydrocarbon and the "% transfer" is reduced to 3-8%. On the other hand, during the reduction of diazonium salt dissolved in ordinary water by heavy hypophosphorous acid (Experiments 13-15), the "% transfer" becomes very high, reaching 200%.

These observations can only be explained by the fact that the above-indicated assumption concerning the possibility of instantaneous exchange of the hydrogen of the P−H bonds of hypophosphorous acid is erroneous. In actuality, these hydrogen atoms are exchanged more slowly than the rate at which the reduction reaction proceeds. In the first experiments (Experiments 10-12) the hydrocarbon is obtained primarily at the expense of the light hydrogen of the P−H bonds of hypophosphorous acid, which is not successfully exchanged for deuterium. On the other hand, in Experiments 13-15, the hydrocarbon is obtained primarily from the P−D bonds of the heavy hypophosphorous acid, which also is not successfully exchanged for the ordinary hydrogen of the water. Establishment of the fact of slow exchange of these hydrogen atoms which are transferred to the diazonium salt radical simultaneously resolves the question concerning the source of these hydrogen atoms, since it is well known that hydrogen

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*The solution was obtained by saturating an aqueous solution of sodium hypophosphite with dry hydrogen chloride. The sodium chloride formed was filtered off. To obtain heavy hypophosphorous acid a known quantity of deuterium oxide was added to the solution and the mixture was left to stand at room temperature for a prolonged time.

**For various experiments. A purer product which would have given a better yield in these experiments, could have been prepared.

TABLE 2

Reduction of p-Toluyldiazonium Chloride by Hypophosphorous Acid*

Experiment No.	Quantity of H_3PO_2 (in g)	Quantity and increment in density of water				Increment in density of water (in γ)			% transfer of deuterium
		for H_3PO_2 solution		for diazonium salt solution		in the mixture at the end of the reaction d_e	average $d_{av.}$	water from the combustion of the hydrocarbon · 8 d_h	
		(g)	(γ)	(g)	(γ)				
1	55	25	0	103	3100	2280	2690	370	14
2	61	27	0	90	3700	2540	3120	270	9
3a	61	27	0	90	3700	2540	3120	460	15
4b	91	57	3870	31	3700	3280	3490	430	12
5c	62	28	3860	22	2000	2380	2190	370	17
6	88	40	0	150	2000	1430	1710	185	11
								335	20
								410	24
7d	61	27	4320	20	1500	2410	1950	700	36
8e	46	21	4320	20	1500	2360	1930	810	42
9e	62	28	3940	75	3260	3030	3150	1000	32
10	61	27	0	100	2920	2070	2490	80	3
11	55	25	0	100	1720	1250	1480	120	8
12	66	30	0	100	2170	1500	1830	120	6
13	56	26	7970	75	0	1830	910	1640	180
14	56	26	3430	100	0	640	320	600	190
15	57	27	4930	60	0	1340	670	905	140

atoms entering into the O—H bond of hypophosphorous acid, as in any other compound [4, 5], instantaneously exchange with the deuterium of heavy water. Consequently, it is hydrogen atoms bound through the phosphorous of the hypophosphorous acid which are transferred to the hydrocarbon radical of the diazonium salt.

Three series of experiments were conducted. In the first series (Experiments 1-6) solutions of diazonium salts in heavy water were reduced with ordinary hypophosphorus acid or with hypophosphorous acid which had preliminarily been placed in contact with heavy water for a duration of 10-15 minutes in all. The results obtained are evidence of the fact that during such an experimental arrangement of experiments, the percent transfer of deuterium into toluene varies from 9 to 17. It is necessary to discuss the results of Experiment 6 separately. This experiment differed from the others in the fact that the toluene was not isolated all at once and as a whole from the reaction mixture after completion of the reaction, but in portions as the toluene was formed, in quantities sufficient for conducting analyses. Three samples of toluene in all were taken; the two last samples, as is evident from Table 2, contained more deuterium than the first. This is readily explained by the fact that the formation of toluene in the two last samples proceeded by means of reaction of the diazonium salt with hypophosphorous acid, which had already succeeded to a considerable extent in exchanging its hydrogen atoms of the P—H bonds for deuterium of the heavy water.

In the second series of experiments (Experiments 7-9) the solution of diazonium salt in heavy water was reduced with hypophosphorous acid which was preliminarily placed in contact with heavy water for a duration of many hours (from 47 to 96 hours) at room temperature. Comparison of the results obtained in the first series of experiments with the results of the second series shows that reduction of the diazonium salt with hypophosphorous acid placed for a prolonged period in contact with heavy water leads to an increase in the content of deuterium in the toluene being formed by a factor of almost two, in comparison with the toluene obtained by the reduction of diazonium salt with hypophosphorous acid not containing deuterium at the beginning of the reduction reaction or placed in contact with heavy water insufficiently long for substantial exchange of all the hydrogen atoms in the molecule.

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* a Temperature of the reaction mixture 35-45°.

Time of preliminary contact between the water and hypophosphorous acid:

b 10 minutes

c 15 minutes

d 47 hours

e 91 hours

In Experiment 6 the first sample was taken after 1 hour 50 minutes, the second after 3 hours 50 minutes, the third after 24 hours.

Experiments 9-15 were conducted in the presence of cupric sulfate; the remaining experiments—without catalyst.

In follows from this that the exchange of those hydrogen atoms of hypophosphorous acid which participate in the formation of the hydrocarbon does not proceed instantaneously, but at a rate not very markedly different from the rate of the reduction reaction.

For a still more definite clarification of the source of the hydrogen, it was evidently necessary to accelerate the reduction process without simultaneously accelerating the rate of the exchange reaction. Raising the reaction temperature did not bring this about.

We succeeded in achieving the desired result by catalyzing the reduction reaction with cupric sulfate [24]. The experiments of the third series (Experiments 9-15) were conducted analogously to the first two series but in the presence of catalyst. Toluene was extracted from the mixture 10 minutes after the beginning of the mixture of the reagents; the mixing process took about 5 minutes. The results obtained are evidence of the fact that during the addition of ordinary hypophosphorous acid to a solution of diazonium salt in heavy water in the presence of cupric sulfate (Experiments 10-12), toluene containing very little deuterium is formed. The percent of transfer of deuterium in this case is low, which is evidence of the fact that the bulk of the toluene is formed at the expense of the hydrogen of the P—H bonds of the hypophosphorous acid which has not succeeded in exchanging its hydrogen for the deuterium of the water. If the exchange had proceeded prior to the reduction reaction, then the percent transfer of deuterium would have been equal to approximately 30-35 (Experiment 9, Exps. 7 and 8 in part, Table 2 in which exchange does not complicate the picture). On the contrary, during the reduction of a solution of diazonium salt in ordinary water by heavy hypophosphorous acid (Experiments 13-15) the percent transfer of deuterium is very high, which is again evidence of the transfer to the toluene of deuterium from the heavy hypophosphorous acid which successfully exchanged the P—D bonds.

The results of the experiments, which are summarized in Table 2, permit us to make a rough computation of the ratio of the rates of exchange and of reduction. Let us assume that this ratio of rates amounts to:

$$\frac{V_{\text{exch.}}}{V_{\text{red.}}} = \frac{1}{n}.$$

It is readily seen that of $\underline{m}$ hypophosphorous acid molecules $\frac{m}{n+1}$ are exchanged prior to the act of reduction and reduce $\frac{n \cdot m}{n+1}$ molecules of diazonium salt without exchange, since the comparative rates of exchange and reduction are equal to $\frac{1}{n+1}$ and $\frac{n}{n+1}$, respectively. The average isotopic composition of the hydrogen of the hypophosphorous acid which is transferred to the hydrocarbon, $\underline{d}$ will be equal to

$$d = \frac{\frac{n \cdot m}{n+1} \cdot d_d + \frac{m}{n+1} \frac{d_w + d_e}{2}}{m}$$

or

$$d = \frac{n \cdot d_d + d_{\text{av.}}}{n+1},$$

where d_d is the initial deuterium content in the P—H bonds of hypophosphorous acid (the donor), d_w is the deuterium content in the water employed to dissolve the diazonium salt, d_e is the deuterium content in the final reaction mixture and $d_{\text{av.}}$ is half the sum of the values of d_w and d_e.

The percent transfer of deuterium if the exchange reaction is excluded is equal to 32 (Experiment 9). Taking this percent transfer of deuterium into account, it is readily found that there should be 0.32 d deuterium

TABLE 3

Experiment No.	Group	n
1	I	1.3
2		2.7
3		1.2
4		1.6
5		0.9
6		1.4
10	II	10.0(?)
11		3.0
12		3.9
13	III	1.4
14		1.0
15		1.0

in a single position of the hydrocarbon. Experimentally we find values equal to d_h (next to the last column of Table 2). This makes it clear that it is possible to construct an equation to determine n. It will have the form:

$$d_h = 0.32 \cdot d, \text{ or } d_h = 0.32 \cdot \frac{nd_d + d_{av.}}{n + 1}. \qquad \text{(I)}$$

Placing the values for the density of water from Table 2 in formula (I), we find (in reduction with light hypophosphorous acid $d_d = 0$) quantities which are presented in Table 3.

It follows from these data that for the reduction reaction with light hypophosphorous acid without catalyst (Group I) the quantity n is on the average close to 1.5. For reduction with light hypophosphorous acid in the presence of cupric sulfate (Group II) n is close to 4 and for reduction with heavy hypophosphorous acid in the presence of cupric sulfate (Group III) n is slightly above 1. It is evident that these computations have only a tentative character; however, for all that, they apparently give the correct order of magnitude of the unknown quantities.

Consequently, in the absence of catalyst the rate of exchange is only a little less than the rate of reduction (approximately one and half times). However, in the presence of catalyst which accelerates the rate of reaction, the exchange proceeds considerably slower than the reduction (approximately 4 times). The reversible exchange reaction has a rate of the same order of magnitude as the rate of the reduction with heavy hypophosphorous acid.

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SUMMARY

1. The hydrogen of the C—H bonds of alcohol and of the P—H bonds of hypophosphorous acid was transferred to the hydrocarbon radical of diazonium salts.

2. Deuterium at the P—H bond of hypophosphorous acid is transferred to the compound being reduced approximately 3 times more slowly than hydrogen.

3. In the absence of catalyst the rate of exchange of hydrogen at the P—H bonds of hypophosphorous acid is somewhat less than the rate of reduction. In the presence of cupric sulfate the rate of reduction considerably increases and the exchange reaction proceeds approximately 4 times slower than the reduction reaction.

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INVESTIGATION OF THE MIGRATION ROUTES OF THE HYDROGEN ATOM DURING CERTAIN OXIDATION-REDUCTION REACTIONS. II

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In the preceding work [1] the results of our experiments on the reduction of diazonium salts with ethyl alcohol and hypophosphorous acid containing the heavy isotope of hydrogen—deuterium, were communicated. In this communication the results of investigations of the reaction mechanism of the reduction of diazonium salts with formaldehyde, the reduction of aldehydes with ethyl alcohol in the presence of aluminum ethylate, and the oxidation of phenylhydrazine with cupric sulfate and potassium ferricyanide will be summarized. The mechanism of these reactions was studied with the aid of the heavy isotope of hydrogen.

Reduction of Diazonium Salts with Formaldehyde*

We saw [1] that in the reduction of diazonium salts with ethyl alcohol and hypophosphorous acid the radicals of the diazonium salts in the process of forming benzene derivatives take up hydrogen from the weaker C—H or P—H covalent bonds but not from the stronger polar O—H bonds of the reducing agent. Analogously (see below) during the oxidation of phenylhydrazine, hydrogen is transferred to the phenyl radical from the N—H but not from O—H bonds.

One might suppose that the reduction of diazonium salts with formaldehyde dissolved in heavy water would lead to the formation of reaction products not containing deuterium, since the radicals of the diazonium salt will take up the less strongly bound hydrogen of the C—H bonds of the formaldehyde and not the deuterium of the O—H bonds of the reaction medium.

Actually, however, we detected that the products formed contain a considerable quantity of deuterium and, consequently, the reduction of diazonium salts with formaldehyde proceeds by a different mechanism than the reduction by alcohol or hypophosphorous acid.

The experiments were conducted in the following manner [3]. Dry diazonium salts obtained in the usual way were dissolved in diluted heavy water cooled to 0°, and 40% formaldehyde (d 1.15) and potassium hydroxide (about 40 ml and 25 g, respectively, per 0.2 mole of diazonium salt) in dilute heavy water were added in drops to the solution. The reaction products were either distilled off from the reaction mixture or extracted from it with ether. After the usual purification and drying the reaction products were fractionated: benzene b.p. 79.5-80°, n_D^{21} 1.5002-1.5012; toluene b.p. 109.5-110.5°, $n_D^{20.5}$ 1.4945-1.4955; anisole b.p. 153-154°, n_D^{21} 1.5170-1.5175,** and burned.

The conditions of the experiments and the results of the analyses of the water from the combustion are set forth in Table 1. In Column 6 of this table are set forth the data concerning the increment in the density of the water in the initial reducing mixture (calculated with an allowance for the dilution with heavy water of the water in the formaldehyde solution). As the reaction proceeded diazonium salt was added to the reducing mixture. The increment in the density of water corresponding to this at the end of the reaction was somewhat different (Column 7). The arithmetic means of the quantities in Columns 6 and 7 are given in Column 8.

The content of deuterium in one particular position of the molecule (Column 9) was determined by multiplying the observed density of the water from its combustion by the total number of hydrogen atoms (m̲) in the given compound. As previously [1], we denote the ratio of the quantities set forth in Columns 9 and 8 as the percent transfer of deuterium (Column 10).

It is evident from the data of Table 1 that the percent of transfer of deuterium varies from 19 to 34 during the formation of various hydrocarbons and of anisole. The causes of these variations were not clear to us and will be explained in what follows.

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* For a brief note on this see [2].

** For compounds obtained in various experiments.

The presence of deuterium in the compounds being formed indicates that the formaldehyde hydrogen atoms do not transfer directly to the diazonium salt radical. In all probability it was to be assumed that the formaldehyde hydrogen is initially transferred to some intermediate compound formed by the incomplete reduction of the diazonium salt, and adds to this latter at the nitrogen atom. As is well known, hydrogen in N–H bonds is rapidly exchanged with the deuterium of water; therefore, during the further conversions of the indicated intermediate compound it would not be the initial light hydrogen of formaldehyde which would be transferred to the radical of the diazonium salt but the exchanged hydrogen having the same isotopic composition as the hydrogen of the reaction medium. Deuterium, therefore, appears to be present in the compound being formed.

TABLE 1

Reduction of diazonium salts by formaldehyde in alkaline medium

Experiment No.	Quantity and density increment of water				Increment in the density of water (in γ)				Percent transfer of deuterium
	for the salt solution		for the reducing mixture		in the initial reducing mixture	in the mixture at end of the reaction	average	water from the combustion of the hydrocarbons	
	(g)	(γ)	(g)	(γ)	calculated			m	
1	2	3	4	5	6	7	8	9	10
					Reduction of phenyldiazonium chloride				
1	20	1950	80	1950	1430	1510	1470	370	25
2	60	1130	140	1130	810	860	830	200	24
3	30	1200	75	1200	830	910	870	180	21
4	30	1200	75	1200	830	910	870	160	19
								Average	22
					Reduction of p- and o-toluyldiazonium chloride				
p-7	10	0	50	2740	2160	1870	2020	730	36
p-6	10	0	70	2740	2310	2070	2190	670	31
p-9	10	0	70	2740	2310	2070	2190	830	38
p-10	12	0	70	2240	1870	1660	1760	590	34
p-11	10	2740	50	2740	2160	2240	2200	840	38
p-12	12	2740	70	2740	2330	2380	2360	610	26
p-13	30	1130	71	1130	770	850	810	350	43
p-14	20	1490	80	1490	1060	1110	1080	380	36
o-17	20	1490	80	1490	1060	1110	1080	310	29
o-18	20	1200	80	1200	850	910	880	260	30
								Average	34
					Reduction of p-anisyldiazonium chloride				
19	22	1200	80	1200	840	900	870	160	18
20	20	1490	80	1490	1050	1110	1080	220	20
								Average	19

It is well known that diazonium salts form hydrocarbons when reduced by arylhydrazines. On the basis of this observation a hypothesis has been advanced to the effect that in every other method of reducing diazonium salts to hydrocarbons, reaction of the unreacted diazonium salts with an intermediately formed arylhydrazine takes place. If this hypothesis were shown to be correct then during the reaction of phenyldiazonium chloride with phenylhydrazine one would expect the formation of hydrocarbons with the same percent transfer of deuterium as during the reduction of phenyldiazonium chloride with formaldehyde. This has not been confirmed experimentally. The percent transfer of deuterium in benzene during the reaction of phenyldiazonium chloride with phenylhydrazine turned out on the average to be equal to 42% in place of 22% during the reduction of phenyldiazonium chloride by formaldehyde.

These experiments were conducted in the following manner. Phenyldiazonium chloride was dissolved in heavy water and added to a solution of potassium hydroxide also in heavy water. A suspension of phenylhydrazine in heavy water was added to the diazotate solution thus obtained. The mixture was stirred mechanically and cooled with ice. After completion of the reaction benzene was steam distilled off, dried, fractionated (b.p. 79.5-80.0°, n_D^{22} 1.5012), and burned over cupric oxide. The quantity of reagents and the results of the experiments are set forth in Table 2.

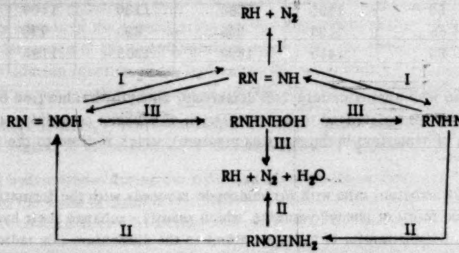
TABLE 2

Reduction of phenyldiazonium chloride by phenylhydrazine in alkaline medium

Expt. No.	Quantity and density increment of water				Increment in the density of water (in γ)				Percent transfer of deuterium
	for the solution of diazonium salt		for the phenylhydrazine solution		in the initial diazotate solution	in the mixture at end of the reaction	average	water from the combustion of the benzene · 6	
	(g)	(γ)	(g)	(γ)	Calculated				
1	40	2530	10	2530	2380	2300	2340	1050	45
2	50	2530	10	2530	2410	2330	2370	920	39
3	103	1040	20	1040	1020	1000	1010	445	44
4	73	1130	30	1130	1090	1070	1080	430	39

The marked difference in the percentages of transfer of deuterium found during the formation of benzene from phenyldiazonium chloride by its reduction with formaldehyde (22%) and phenylhydrazine (42%) compels us to assume that the reduction of the diazonium salt with formaldehyde, in any case for the basic mass of the salt, does not proceed through a stage of intermediate formation of phenylhydrazine.

We consider the following to be the most probable general scheme for reversible oxidation-reduction conversions of diazocompounds and arylhydrazines:*



(Scheme A)

According to this scheme, the intermediate compounds during the reduction of diazonium salts and the oxidation of arylhydrazines should be considered to be α- and β-hydroxyphenylhydrazines and aryldiimines. Depending on the reaction conditions and the oxidation-reduction potentials of the reagents, these intermediate compounds can either undergo further oxidation-reduction conversions without loss of nitrogen, or can be decomposed with evolution of hydrocarbons.

During the oxidation of phenylhydrazine with cupric sulfate in heavy water we observed (see below) the formation of benzene with a percent transfer of deuterium to hydrocarbon close to the percent transfer found during the reduction of phenyldiazoniumchloride by formaldehyde. This supports the hypothesis that both reactions actually proceed through similar intermediate compounds.

The course of the process of reduction of diazonium salts by formaldehyde can presumably be depicted by such a sequence of reactions as the following:

a) addition of two formaldehyde hydrogen atoms to the diazotate (Course III, Scheme A) and

b) mono- or bimolecular decomposition reaction of β-hydroxyphenylhydrazine with evolution of benzene.

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* For a similar scheme in less general form see also the earlier [5, 6].

In the course of investigation of the oxidation of phenylhydrazine in acidic and alkaline media (see below) we showed that the phenyl radical forms benzene at the expense of the N—H bonds of compounds present in the system, but not at the expense of their O—H bonds. It can be supposed that an analogous process also takes place in the given case. Stage (b) is assumed just on the basis of analogy with the reactions under consideration.

During the reaction of phenyldiazotate with phenylhydrazine the latter, according to our data, conducts itself just like formaldehyde, reducing the diazotate to phenyldiimine:

$$\begin{tikzcd}[column sep=small] RNHNH_2 + RN{=}NOH \arrow[r] & RN{=}NH \arrow[d] & + & RNHNHOH \arrow[d] \\ & RH + N_2 & & RH + N_2 + H_2O \end{tikzcd}$$

Further, both intermediate compounds are decomposed independently of each other.

TABLE 3

Reduction of diazonium salts by formaldehyde in the presence of copper salts

Expt. No.	Quantity and density increment of water				Increment in the density of water (in γ)				Copper salt
	for the solution of diazonium salt		for the reducing mixture		in the initial reducing mixture	in the mixture at end of the reaction	average	water from the combustion of hydrocarbons and anisole*	
	(g)	(γ)	(g)	(γ)					
B-1	34	1010	90	1050	795	845	815	0	$CuSO_4$
B-2	30	1385	70	1385	900	1000	950	2	$CuSO_4$
B-3	50	1495	70	1495	960	1130	1045	9	Cu_2Cl_2
B-4	50	1700	65	1700	1030	1200	1115	0	$CuSO_4$
B-5	50	1700	65	1700	1060	1260	1160	6	Cu_2Cl_2
B-6	50	1700	65	1700	1060	1260	1160	10	Cu_2Cl_2
PT-1	20	1490	80	1490	1060	1130	1100	5	$CuSO_4$
PT-2	25	1130	55	1130	705	830	770	3	$CuSO_4$
PA-1	20	1490	80	1490	1090	1300	1195	3	$CuSO_4$

Phenyldiazotate yields benzene with approximately 20% deuterium, phenylhydrazine (see below) – with approximately 75% deuterium. On the average this should lead to the preparation of benzene containing about 50% deuterium (from the equilibrium concentration of denterium in the reaction medium), which is close to the quantity found experimentally.

Thus, the reduction of diazonium salts with formaldehyde proceeds with the formation of intermediate compounds, hypothetically oxidized forms of phenylhydrazine, which readily exchange their hydrogen atoms for the deuterium atoms of heavy water. Direct transfer of hydrogen atoms to the diazonium salt radical does not occur.

The routes of hydrogen transfer during this reaction is markedly changed by the addition to the reaction mixture of small quantities of salts of mono- or divalent copper (the latter, in all probability, is reduced by formaldehyde to the monovalent form). The results of the experiments are set forth in Table 3.

It is evident from the data set forth that direct transfer of hydrogen from formaldehyde to the diazonium salt radical takes place in this case.

The mechanism of this catalytic reaction is apparently clearer than that of reactions without catalyst. It can be portrayed by a scheme similar to that of Waters [7] for the Sandmeyer reaction:

$$RN_2^+ + Cu^+ \longrightarrow R\cdot + N_2 + Cu^{++}$$

$$R\cdot + HCHO \longrightarrow RH + \cdot CHO$$

$$\cdot CHO + Cu^{++} \longrightarrow \overset{+}{C}HO + Cu^+$$

$$\overset{+}{C}HO + OD^- \longrightarrow HCOOD$$

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* Making allowance for the usual errors of our measurements (5–10 γ, most frequently in the direction of overestimation) these data are evidence of the absence of deuterium in the compounds. The experiments with phenyldiazonium chloride are designated by the letter B, the experiments with p-toluyldiazonium chloride by the letters PT, and the experiments with p-anisyldiazonium chloride by the letters PA.

We think that the division of the process into separate stages with the participation of free radicals is not to be considered obligatory. A very probable variant of this mechanism can be presented in a scheme involving the participation of reaction complexes which do not evolve free radicals in solution.

It was established by special experiments that neither under the reaction conditions nor in considerably more severe conditions (100°, prolonged time) does formaldehyde practically exchange its hydrogen atoms for the deuterium of heavy water.

One would suppose that the influence of copper salts consists in the simple acceleration of the decomposition reaction of the intermediate oxidized forms of phenylhydrazine, so that the latter does not succeed in exchanging its hydrogen atoms with the deuterium of the heavy water and that, consequently, deuterium is not found in the reaction product.

The results of our experiments, communicated below, show, however, that even at 100° the oxidation of phenylhydrazine in heavy water proceeds with the formation of heavy benzene, i.e., that even under these extreme conditions the exchange manages to proceed to a considerable extent.

The results of this portion of the work indicate that the reduction of diazonium salts by formaldehyde proceeds with the intermediate formation of compounds which quickly exchange their hydrogen atoms. In the presence of salts of mono- and divalent copper, however, direct transfer of hydrogen from the C—H bonds of formaldehyde to the hydrocarbon radicals of the diazonium salts proceeds. The indicated change in the mechanism of one particular reaction under the influence of catalyst merits further study. We have demonstrated previously [1] that the reduction reaction of diazonium salts by hypophosphorous acid in the presence of copper salts proceeds at the expense of the hydrogen of the P—H bonds of the latter. We do not have sufficient basis for assuming that this reaction would proceed by another mechanism in the absence of catalyst, i.e., similarly to the reduction reaction with formaldehyde, which is accomplished at the expense of formation of some intermediate compounds. This question must be studied in more detail in the future.

Oxidation of Phenylhydrazine by Cupric Sulfate and Potassium Ferricyanide*

The object of this portion of the investigation was the study of the oxidation of phenylhydrazine into benzene and the elucidation of the source of the hydrogen which enters into the benzene nucleus. In addition, taking into consideration that the oxidation reaction of arylhydrazines and the reduction of diazonium salts can be considered under certain conditions as two coupled reactions of one and the same oxidation-reduction process [5] $RN_2X \xrightarrow{\text{reduction}} RNHNH_2$; $RNHNH_2 \xrightarrow{\text{oxidation}} RN_2X$, we hoped in this way to arrive at the elucidation of the question of the mechanism of the reduction of diazonium salts by formaldehyde.

The formation of hydrocarbons during the reduction of diazocompounds and the oxidation of arylhydrazines can proceed through one and the same or similar intermediate products, as can be seen in the scheme set forth above for the oxidation-reduction conversions of diazocompounds and arylhydrazines (Scheme A).

The oxidation of phenylhydrazine in aqueous solutions by cupric sulfate [9] and by potassium ferricyanide [10] has been experimentally investigated; consequently, in the present work we also employed these oxidizing agents, substituting water containing 1-3% deuterium for ordinary water.

The source of the hydrogen transferred to the phenyl radical of phenylhydrazine in the reaction under investigation can be either water molecules or the hydrazo groups of the phenylhydrazine itself (or intermediate products of its oxidation).

The hydrogen of N—H bonds is ordinarily exchanged very rapidly for the deuterium of heavy water [11, 12], and therefore, the question of a choice between N—H- and O—H-bonds can arise only in the case of commensurability of the rates of the reaction of oxidation of phenylhydrazine and of isotopic exchange. If the rates of both processes are commensurable, then the composition of the reaction products should depend (by analogy with the experiments of reducing diazonium salts with hypophosphorous acid [1]) on whether heavy phenylhydrazine reacts with a solution of oxidizing agent in water of normal isotopic composition or whether light phenylhydrazine reacts with a solution of oxidizing agent in heavy water.

In conformity with this, the phenylhydrazine oxidation experiments were conducted in the following manner.

1. Oxidation by Cupric Sulfate. In the first series (Experiments 1-6, Table 4) a solution of 11 g of phenylhydrazine in 10 ml of acetic acid, diluted with ordinary water, was poured into a boiling solution of cupric sulfate,

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* B. E. Gruz participated in this portion of the work; see the preliminary communication [8].

taken in 10% excess, in heavy water. In the second series (Experiments 7-11, Table 4) a solution of 11 g of phenylhydrazine in heavy water and ordinary acetic acid (10 ml) was poured in drops into a solution of $CuSO_4$ in ordinary water. Benzene was distilled off from the reaction mixture as it was formed. After the usual drying and purification the benzene was fractionated (b.p. 79.5-80°, n_D 1.4995-1.5000) and burned. The data are set forth in Table 4.

2. **Oxidation by Potassium Ferricyanide** was conducted in the cold. Phenylhydrazine in the form of an aqueous suspension was poured into an alkaline solution of the oxidizing agent. Benzene was distilled off from the reaction mixture after the completion of the reaction. The order of addition of reagents and of purification of the benzene obtained was the same as in the cupric sulfate oxidation experiments. The data are set forth in Table 5.

TABLE 4

Oxidation of phenylhydrazine by cupric sulfate in acidic solution

Expt. No.	Quantity of phenylhydrazine (in g)	Quantity of water and its density increment				Increment in the density of water (in γ)				Percent transfer of deuterium
		for the phenylhydrazine solution		for the oxidizing agent solutions		in the initial oxidizing mixture	in the mixture at end of reaction	average	in water from the combustion of the benzene X 6	
		(g)	(γ)	(g)	(γ)	Calculated				
1	11	10	0	80	3060	3060	2610	2840	630	22
2	11	10	0	80	3060	3060	2610	2840	540	19
3	11	10	0	80	3160	3160	2680	2920	640	22
4	11	10	0	80	3160	3160	2680	2920	600	21
5	10	10	0	100	2960	2960	2600	2780	490	18
6	10	10	0	100	2960	2960	2600	2780	550	20
7	11	50	3060	80	0	0	1140	570	240	42
8	11	50	3160	80	0	0	1180	590	210	36
9	11	80	2960	40	0	0	1900	950	440	46
10	10	30	2960	100	0	0	660	330	160	49
11	10	30	2960	100	0	0	660	330	150	45
12	22	35	1530	75	2150	1940	1720	1830	360	20*
13	22	32	1130	60	1130	1020	970	990	280	28**
14	11	60	1450	60	1490	1450	1380	1420	380	27

TABLE 5

Oxidation of phenylhydrazine by potassium ferricyanide in alkaline solution

Expt. No.	Phenylhydrazine (g)	Quantity of water and its density increment				Increment in the density of water (in γ)				Percent transfer of deuterium
		for the phenylhydrazine solution		for the oxidizing agent solutions		in the initial oxidizing mixture***	in the mixture at end of reaction	average	in water from the combustion of the benzene X 6	
		(g)	(γ)	(g)	(γ)	Calculated				
1	11	40	0	80	3060	2960	1940	2450	1510	61
2	11	30	0	59	3060	2930	1890	2410	1500	62
3	10	70	0	80	2240	2170	1150	1660	1050	63
4	10	70	0	80	2240	2170	1150	1660	1170	70
5	10	70	0	80	2070	2010	1070	1540	1030	67
6	10	70	0	80	2070	2010	1070	1540	1030	67
7	11	80	2960	40	0	0	1880	940	900	96
8	11	80	2830	40	0	0	1800	900	1030	115
9	11	80	2830	40	0	0	1800	900	940	105
10	10	30	2240	120	0	0	440	220	300	136
14	22	20	1010	180	1010	990	960	975	750	77
15	11	70	1030	121	1030	1010	990	1000	720	72
16	11	10	1020	125	1020	990	970	980	720	74

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* 40 ml of 96% ethanol was added to the aqueous $CuSO_4$ solution.

** 50 ml of the absolute ethanol was added to the aqueous $CuSO_4$ solution.

*** Making allowance for exchange with the added potassium hydroxide.

In the last columns of Tables 4 and 5 are set forth values expressing the ratio of the experimentally found content of deuterium in benzene (in one position) to the calculated average of the equilibrium content of deuterium in all the hydrogen atoms of the reaction mixture which are capable of exchanging.

As we have previously demonstrated [1], the magnitudes of the percent of transfer of deuterium obtained in this way characterize the actual ratio of the rates of transfer of deuterium and hydrogen in the reaction under investigation only when the contents of deuterium in the O—H groups of the water and the N—H groups of the phenylhydrazine are identical, i.e., under conditions in which the isotopic exchange does not lead to change in the isotopic composition (Experiment 14, Table 4; Experiments 14-16, Table 5), or proceeds instantaneously.

It is evident from comparison of the data obtained in Experiments 1-6 and 7-11 of Table 4 that the average percent of transfer of deuterium during the oxidation of light phenylhydrazine by cupric sulfate solution amounts to 21%. The percent of transfer is raised to 44% in the oxidation of heavy phenylhydrazine by a solution of the oxidizing agent in ordinary water. The data of experiment 14 show that the percent of transfer of deuterium during the addition of heavy phenylhydrazine to a solution of the oxidizing agent in heavy water amounts to 27%.

The change of the magnitudes of the percent of transfer with changes in the sequence of introduction of heavy water can be explained by the fact that the exchange reaction during the oxidation of phenylhydrazine does not proceed instantaneously, but at a rate commensurable with the rate of the oxidation reaction. During the oxidation of light phenylhydrazine a portion of the benzene is formed from incompletely-exchanged compound. This results in a lower content of deuterium (low percent of transfer) in the hydrocarbon. Exactly as in the oxidation of heavy phenylhydrazine the benzene is partially formed from this latter. This leads to an increased deuterium content in comparison with that calculated (complete exchange prior to the oxidation reaction).

A similar pattern is also observed during the oxidation of phenylhydrazine by potassium ferricyanide in alkaline medium. In this case the percent transfer of deuterium during the addition of light phenylhydrazine to a solution of the oxidizing agent in heavy water (Experiments 1-6, Table 5) is equal to 65, while during the oxidation of heavy phenylhydrazine by a solution of the oxidizing agent in ordinary water (Experiments 7-11, Table 5) it becomes even higher than 100. In the absence of exchange between the phenylhydrazine and the reaction medium (Experiments 14-16, Table 6) the percent transfer of deuterium is on the average equal to 74.

The results obtained are thus evidence of the fact that during the oxidation of phenylhydrazine by cupric sulfate and potassium ferricyanide, benzene is formed at the expense of the hydrogen atoms of the N—H bonds of phenylhydrazine. The picture is strongly obscured by isotopic exchange, but this conclusion can, on the whole, be considered quite well founded.

The results obtained are also of interest since they open up the possibility of evaluating the rates of rapid exchange reactions which cannot successfully be determined by ordinary methods. The separation of exchanging substances ordinarily requires at least several minutes, and, consequently, it is difficult to evaluate correctly the degree of exchange in periods not exceeding 1-2 minutes. In cases similar to that under investigation, one can set up a model of the exchange between substances that are in contact for a matter of seconds.

Using the formula (I) linking the rates of the exchange and oxidation reactions [1], the ratio of these rates can readily be found for the phenylhydrazine oxidation experiments with both cupric sulfate and potassium ferricyanide. The corresponding values of $\underline{n}$ are set forth in Table 6.

The precision of the determinations of the magnitudes of $\underline{n}$ is not great, and we cannot verify that the magnitudes of $\underline{n}$ for differing conditions of the oxidation of phenylhydrazine are actually different from each other. Taking $n = 0.2$, we obtain the result that the rate of the exchange reaction in all the oxidation reactions studied by us is approximately 5 times greater than the rate of the oxidation reaction.

The data obtained by us are thus evidence of the fact that hydrogen is transferred to the phenylhydrazine radical from its N—H bond and not from the hydrogen of water.

The marked difference in the observed percents of transfer of deuterium during the oxidation of phenylhydrazine with cupric sulfate, on the one hand, and with potassium ferricyanide, on the other (27% and 74%) under conditions in which the exchange between the starting material and the reaction medium does not change their isotopic composition, confirms the hypothesis advanced by Kizhner [13] concerning the differing mechanisms of the oxidation of hydrazines when these two oxidizing agents are used.

We assume that the oxidation of phenylhydrazine proceeds according to the following mechanism.

TABLE 6
Oxidation of phenylhydrazine

Experiment No.	Cupric sulfate n	Potassium ferricyanide n
1	0.22	0.20
2	0.42	0.19
3	0.23	0.17
4	0.31	0.05 (?)
5	0.53	0.11
6	0.37	0.11
7	0.16	0.17
8	0.09	0.37
9	0.58 (?)	0.26
10	0.13	0.11
11	0.11	–

In acidic medium cupric sulfate oxidizes phenylhydrazine to *a*-hydroxyphenylhydrazine (Course II, Scheme A). The introduction of a hydroxyl group in the *a*-position is in agreement with the known facts of enhanced reactivity of the secondary hydrogen atom in phenylhydrazine (in comparison with the primary), noted by Kizhner [13] and others.

Homolytic decomposition of the oxidized forms of phenylhydrazine subsequently takes place in the reaction complex without evolution of free radicals in the solution. This ensures migration of hydrogen atoms from the N–H bonds to the phenyl radical. An ionic decomposition process would result in migration of the hydrogen from the more polar O–H bonds.

The oxidation of phenylhydrazine not containing deuterium and the decomposition of the corresponding molecules of *a*-hydroxyphenylhydrazine require less activation energy, and consequently proceed primarily before the cleavage of the heavy compounds. This explains the low percent deuterium transfer to benzene found by us. We found values of the percent transfer of deuterium equal to 20-30, that corresponded to the literature data concerning the ratio of the reaction rates of isotopically different molecules of any given compound equal to 1:3-1:5 and were dependent on the difference of the zero energies of ordinary hydrogen and deuterium compounds. The greater portion of the deuterium-containing intermediate products of the oxidation of phenylhydrazine are converted into the resinous products usually formed during the reaction. An analogous phenomenon, i.e., the accumulation of deuterium in the reaction medium, is observed during the oxidation of heavy isopropyl alcohol $(CH_3)_2CDOH$ by chromic acid [14], during the photochlorination of mixtures of $CHCl_3$ and $CDCl_3$ [15] and so forth.

The results of experiments conducted in the presence of ethyl alcohol favor the assumption that homolytic bond cleavage is not accompanied by formation of free radicals during the oxidation of phenylhydrazine by cupric sulfate (as well as during the reduction of diazonium salts by alcohol and [illegible] and during the photodecomposition of phenylmercury hydroxide [16] in alcohol solution). The benzene obtained in these experiments was of the same isotopic composition as in the absence of alcohol. If there were free radicals present in the reaction medium, then one could expect the formation of light benzene at the expense of the removal of hydrogen from the radicals of the weak C–H bonds of the alcohol.

Our data on the oxidation of phenylhydrazine by potassium ferricyanide are in agreement with the hypothesis of Kizhner [10, 13] concerning an intermediate formation under these conditions of phenyldiimine which is very unstable and is entirely converted into benzene (Course I, Scheme A).

The fact that only one hydrogen atom can fit into the diimine molecule for each phenyl radical and consequently, that there is no possibility of choice between H and D atoms, i.e., the assumption of its complete conversion into benzene, can explain the high percent transfer of deuterium found by us under these oxidation conditions.

The formation of these or other intermediate compounds during the reversible interconversion of diazo compounds and arylhydrazines (Scheme A) depends on the oxidation-reduction properties of the reaction medium [5]. It is, consequently, not surprising that the oxidation of phenylhydrazine by potassium ferricyanide and the reduction of phenyldiazotate by formaldehyde proceed by different mechanisms, although they both proceed in alkaline solution. As we have already said, in the first case the formation of phenyldiimine is assumed and in the second, the formation of *β*-hydroxyphenylhydrazine is assumed.

To exclude the possibility of exchange of hydrogen atoms in the phenylhydrazine nucleus at the time of reaction, several experiments were set up involving exchange with phenylhydrazine in heavy water under conditions of acidic and basic catalysis. As is evident from Table 7, exchange of hydrogen atoms in the phenylhydrazine nucleus for deuterium of heavy water is not observed even under comparatively severe conditions. It is of interest to compare the behavior of phenylhydrazine with that of aniline which exchanges its nuclear hydrogen atoms with considerable rapidity during acidic catalysis [11, 12].

Reduction of Aldehydes by Aluminum Alcoholates*

The question of similarity of the mechanisms of the Cannizzaro and Meerwein reactions has been considered a number of times [18, 19]; it is consequently not devoid of interest to elucidate whether or not there is also a

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*For a brief communication on this subject, see [17].

TABLE 7

Exchange of Phenylhydrazine with Heavy Water in Acidic and Alkaline Media. A. Exchange in Alkaline Medium, 20°.

Duration of exchange	Quantity of D_2O (in g)	Content of D in the initial D_2O (in γ)	Quantity		Content of D in the water from the combustion of phenylhydrazine		Exchange in the $NHNH_2^-$ - group %
			of alkali (in g)	of phenylhydrazine (in g)	Found	Calculated	
2 min.	5.0160	2960	1.6120	8.0700	730	760	96.0
20 min.	4.9355	2960	1.3330	7.9320	770	770	100.0
48 hours	4.9485	2960	1.3318	8.3318	760	755	100.5
105 hours	4.9990	3460	1.3560	7.1045	890	920	96.7
12 hours*	5.0820	3460	1.5405	8.5920	890	885	100.5*

B. Exchange in Acidic Medium, 20°.

Duration of exchange	Quantity of phenylhydrazine (in g)	Solution of acetic acid in heavy water			Content of D in the water from the combustion of the phenylhydrazine (in γ)		Exchange in the $NHNH_2^-$ - group %
		quantity (in g)	content				
			of D in the hydroxyl group (in γ)	of acetic acid in 1 g of solution	Found	Calculated	
1 min.	7.6420	7.7583	2710	0.372	760	740	103
3 min.	8.8710	7.6220	2535	0.322	730	680	107
20 min.	7.4560	8.0765	2710	0.372	800	760	105
27 hours	8.4100	7.2490	2535	0.322	730	680	107
49 hours	8.4110	7.2940	2535	0.322	700	680	103
67 hours	7.5395	7.7909	2710	0.372	800	750	106

TABLE 8

Reduction of Furfural and Benzaldehyde by Aluminum Ethylate in Heavy Ethyl Alcohol

Experiment No.	Weight (in g)			Duration of the reaction (in hours)	Content of deuterium (in γ)			
	Aldehyde	C_2H_5OD	$(C_2H_5O)_3Al$		in the hydroxyl group of ethanol	in the water from the combustion of alcohols	in the C–H bonds of the alcohols	
							according to the analysis of water	calc.
Fur. 1	9.6	16.0	7.0	168	6600	21	126	4600
Fur. 2**	11.6	32.0	7.0	72	6600	28	168	5500
Fur. 3	17.4	24.0	5.0	210	7100	14	84	5500
Benz. 1	15.7	24.0	7.0	168	6600	11	88	5100
Benz. 2**	15.7	30.0	5.0	72	6600	18	144	5400
Benz. 3	15.7	24.0	6.5	144	7100	11	88	5500

congruence between these reactions in connection with the source of the hydrogen of the new C – H bond which arises during the conversion of an aldehyde molecule into a molecule of the corresponding alcohol.

A determined quantity of aldehyde was added to a solution of aluminum ethylate in ethyl alcohol containing deuterium in the hydroxyl group, and the mixture was mixed and left to stand at room temperature in a closed flask. The solvent was distilled off from the mixture after a few days and the residue was steam distilled. The alcohol formed from the aldehyde was extracted from the distillate with ether and after eliminating the latter, was redistilled with a branched fractionating column. Fractions were collected boiling in the ranges 169-172° for furfuryl, and 202-205° for benzyl alcohol.

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*The exchange proceeds at 100°.

Note. In the "calculated" column figures are set forth for the exchange of the three hydrogen atoms of the $NHNH_2$ = group of phenylhydrazine.

**These experiments differ from the others in the fact that the reacting mixtures were boiled for 1 hour with a reflux condenser and after this were left at room temperature for the time indicated in the table.

Fur. = furfuryl alcohol, Benz. = benzyl alcohol.

The alcohols obtained were burned in a stream of air over cupric oxide at 700-800°. The water from the combustion of the alcohols was analyzed for its deuterium content by the flotation method.

Heavy ethyl alcohol was prepared by addition to absolute alcohol of a determined quantity of deuterium oxide. Dehydration of the alcohol was carried on for twenty-four hours with the aid of metallic calcium. A sample of the heavy alcohol was burned over cupric oxide for isotopic analysis.

In the alcohols formed during the reduction of furfural and benzaldehyde, deuterium could be found both in the bonds with carbon and in the hydroxyl group. The presence of the deuterium in the C – H bonds was of interest to us: deuterium was eliminated from the hydroxyl groups of the alcohols by resubjecting them to steam distillation. 10-15 g of alcohol were ordinarily mixed in the distillate with 1000-1500 ml of water. At the same time there could remain, according to calculation, only very little deuterium (5-7 γ) in the hydroxyl groups of the alcohol molecules. The combustion of furfuryl and benzyl alcohols leads to the dilution of the deuterium contained in them by, respectively, 6 and 8 times, which lowers the final correction for the hydroxyl deuterium to a magnitude (1 γ) that is of no importance relative to the accuracy of our measurements (5-10 γ).

Before proceeding to the discussion of the experimental results, it should be emphasized once more that the question of the source of the hydrogen of the hydroxyl groups of furfuryl and benzyl alcohols has not been elucidated by us. Under the experimental arrangement described, its primary source could not in general be established, since the hydroxyl hydrogen atoms of the alcohols being formed are exchanged with those of ethyl alcohol.

A hydrogen atom can migrate to a carbon atom of the aldehydes undergoing reduction either from the carbon atom (I) or from the oxygen atom (II):

$$RCHO + CH_3CH_2OD \xrightarrow{(C_2H_5O)_3Al} RCH_2OD + CH_3CHO, \qquad (I)$$

$$RCHO + CH_3CH_2OD \xrightarrow{(C_2H_5O)_3Al} RCHDOH + CH_3CHO. \qquad (II)$$

If, in the first case, the process of migration of hydrogen from a carbon atom of one molecule to a carbon atom of another proceeds without participation of solvent (i.e., if the hydrogen migrates directly to the carbon), then there will not be any deuterium in the C – H bonds of the molecules of the furfuryl and benzyl alcohols isolated by us.

On the other hand, if hydrogen atoms of the hydroxyl groups of the reducing agent serve as the source of new C – H bonds, or if the solvent participates in the transfer of hydrogen atoms from a carbon atom of the reducing agent to a carbon atom of the aldehyde (as, for example, during the reduction of diazonium salts by formaldehyde), then deuterium should be contained in the C – H bonds of the newly-formed alcohols.

There should be only as much deuterium in the new C – H bonds during the migration of hydrogen from oxygen as there was in the hydroxyl groups of the heavy ethyl alcohol.

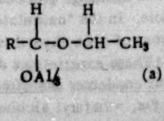
During the carbon-carbon transfer of hydrogen with the participation of solvent, the concentration of deuterium in the C – H bonds should agree with its equilibrium concentration during the complete exchange of all the hydroxyl deuterium atoms and the hydrogen of ethyl alcohol with the migrating hydrogen.

These last quantities are set forth in the column "calculated" of Table 8 in which the results of our experiments are presented.

The data presented in Table 8 leave no doubt that the hydrogen atoms bound to carbon atoms in the reducing agent molecules serve as the source of the hydrogen of the C – H bonds which arise during the reduction of furfural and benzaldehyde, and that the migration of hydrogen from the carbon atoms of one compound to the carbon atoms of another proceeds directly, i.e., without the participation of solvent.

The small increase in the density of the water from the combustion of both alcohols (in comparison with ordinary water) can probably be ascribed to insufficient purification of the water being analyzed, contamination of the alcohols under investigation by deuterium-containing products of side reactions, etc.

The mechanisms proposed up to the present time for the reduction of aldehydes by alcoholates [20] can be roughly divided into two groups. Those mechanisms in which the formation of intermediate compounds of the hemiacetal type (a) is assumed, belong to the first of these groups.



$$R-\underset{OAl_{1/3}}{\overset{H}{C}}-O-\overset{H}{C}H-CH_3 \qquad (a)$$

Those mechanisms which are predicated on the assumption that the reduction process proceeds with the intermediate formation of free radicals [18, 21] can be included in the second group.

The latter assumption has also been discussed in connection with the Cannizzaro reaction.

Kudryavtsev and Shilov [22] recently convincingly demonstrated the catalytic influence of peroxides on the disproportionation of aldehydes.

It is impossible to choose between these mechanisms on the basis of our data since an intramolecular migration of a hydrogen atom from one carbon to another is very probable in the hemiacetal, and this very hydrogen atom would be captured, without participation of the solvent, by radicals during a radical reaction mechanism.

It is important for us that the data obtained are evidence of the participation in the reduction of aldehydes of hydrogen atoms bound to the carbon atoms of the reducing agent and not hydrogen atoms which enter into the composition of the O−H bonds of the compounds present in the system. A similar process of bond homolysis also exists in the Cannizzaro reaction [23].

The authors thank A. I. Brodsky, Member of the Academy of Sciences of the Ukrainian SSR, in whose laboratory these investigations were carried out, for his aid in the work.

SUMMARY

The following conclusions can be drawn on the basis of the results of this and the preceding [1] investigations.

1. During the reduction of diazonium salts and aldehydes by alcohols, hydrogen atoms migrate to the radicals of these compounds from the C−H bonds of the reducing agents.

2. During the reduction of diazonium salts by hypophosphorous acid and the oxidation of phenylhydrazine by cupric sulfate and potassium ferricyanide, the P−H and N−H bonds of the reducing agents serve as the donor of the hydrogen for the compounds being formed.

3. The reduction of diazonium salts with formaldehyde proceeds with the formation of intermediate compounds (probably, oxidized arylhydrazines) which quickly exchange their hydrogen atoms for the deuterium of the water. However, in the presence of catalytic quantities of copper salts the direct migration of hydrogen atoms from the C−H bonds of the reducing agent to the hydrocarbon radicals of the diazo compounds occurs.

4. Several hypotheses concerning the mechanisms of the reactions which were studied and concerning homolytic cleavage processes of bonds in solutions were proposed.

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The latter assumption was also made in connection with [illegible]

Kabachnik and Shatov [illegible] recently convincingly demonstrated the [illegible] of [illegible] cleavage of [illegible]

It is impossible to choose between these [illegible] would be captured without [illegible]

[illegible] of hydrogen atoms [illegible]

The authors thank [illegible] Academy of Sciences [illegible] for his aid in this work.

SUMMARY

1. The [illegible]

During the reduction of [illegible] salts [illegible]

2. During the reduction of [illegible] by cupric sulfate and potassium [illegible] gas hydrogen for the [illegible] found.

3. The reduction of [illegible]

4. [illegible] percentage of [illegible]

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[1] [illegible]

[2] [illegible]

[3] [illegible]

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[18] [illegible]

[19] [illegible]

[20] [illegible] Organic Reactions [illegible]

[21] [illegible]

[22] [illegible]

[23] [illegible] Z. Phys. Chem. [illegible]

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AMIDATION OF CARBOXYLIC ACIDS WITH AMIDES OF PHOSPHORIC ACID

A. V. Kirsanov and E. A. Abrazhanova

It has recently been shown that during the action of various amides of sulfuric acid on carboxylic acids, the corresponding amides of the carboxylic acids are formed in excellent yields, and the mechanism of these reactions was investigated [1]. It is of interest to establish how the amides of other strong mineral acids will react with carboxylic acids, or, in other words, whether the amidation reaction is a specific reaction of sulfuric acid amides or whether it has a more general character and is characteristic of the amides of all strong mineral acids. The reaction of several phosphoric acid amides with carboxylic acids in pyridine solution has been studied in the present work. The reaction was studied in the case of p-nitrobenzoic acid and the following phosphoric acid amides—the trianilide of phosphoric acid, the tri-p-toluidide of phosphoric acid, the trianilide of phenyl sulfonimidophosphoric acid, the dianilide of phosphoric acid, the dianilide of phenylsulfonamidophosphoric acid, the triamide of phenylsulfonimidophosphoric acid and the monoamide of phenylsulfonamidophosphoric acid [2]. Only the trianilide of phosphoric acid appeared to be an amidating agent; all the other phosphoric acid amides failed to react with carboxylic acids in boiling pyridine solution.

In comparing the amides of phosphoric acid and sulfuric acid as amidating agents, the following can be noted.

1. Carboxylic acids are readily amidated by the saturated anilides of both sulfuric and phosphoric acids.

2. The saturated p-toluidide of phosphoric acid does not amidate carboxylic acids. There are as yet no data concerning the properties of the ditolylsulfamide as an amidating agent.

3. The conduct of the unsaturated amides of sulfuric and phosphoric acids is entirely different: phenylsulfamanic acid is a very energetic phenylamidating agent [1], while the dianilide of phosphoric acid does not react with carboxylic acids. In addition, it is necessary to point out that not one of the amides of arylsulfonimidophosphoric acids is an amidating agent.

After it had been established that the trianilide of phosphoric acid amidates p-nitrobenzoic acid, the action of this anilide on other acids was studied. It was shown that the trianilide of phosphoric acid can be employed for the phenylamidation of both fatty and aromatic acids with the same degree of success as diphenylsulfamide.

The reaction proceeds according to the equation:

$$PO(NHC_6H_5)_3 + RCOOH \longrightarrow RCONHC_6H_5 + HOPO(NHC_6H_5)_2.$$

The following were thus obtained: acetanilide (yield 83.1%), the anilide of propionic acid (78.1%), the anilide of stearic acid (90.6%), phenylacetanilide (88.5%), benzanilide (88.9%), and p-nitrobenzanilide (90.9%).

EXPERIMENTAL

Amidation of p-Nitrobenzoic Acid with Various Amides of Phosphoric Acid

A mixture of 0.002 mole of p-nitrobenzoic acid, 0.002 mole of one of the amides of phosphoric acid (enumerated in the general part) and 5.0 ml of dry pyridine was heated in an oil bath at 125° from 2 to 10 hours. The pyridine was distilled off in a vacuum and the remainder was treated as indicated below. Only in the case of the trianilide of phosphoric acid was p-nitrobenzanilide isolated with a yield of 90.9%; in all the other cases neither the amide nor the phenylamide of p-nitrobenzoic acid could be successfully isolated, while the p-nitrobenzoic acid was almost quantitatively re-isolated (95-98%).

Phenylamidation of Carboxylic Acids by the Action of the Trianilide of Phosphoric Acid

A mixture of 0.002 mole of carboxylic acid, 0.002 mole of the trianilide of phosphoric acid (0.65 g) and 5.0 ml of pyridine was heated with a reflux condenser on an oil bath at 120-125° (all the starting materials must be perfectly dry). After heating for five hours the pyridine was distilled off in a vacuum, 10.0 ml of 2 N soda solution was added to the dry residue, the mixture was carefully stirred, the undissolved portion was separated and the residue was washed with water. The unreacted carboxylic acid could be isolated from the filtrate after acidification. The residue was dried and the anilide of the carboxylic acid was extracted from it with ether (to separate it from the phosphoric acid trianilide which did not enter into the reaction and which is insoluble in ether). The ether was distilled off and the anilide was recrystallized.

Thus, the following were obtained:

Acetanilide with a yield of 0.23 g (83.1%), after recrystallization from water, m.p. 112-113°;

The anilide of propionic acid with a yield of 0.23 g (78.1%), after recrystallization from water, m.p. 103-104°;

The anilide of stearic acid with a yield of 0.65 g (90.6%), after recrystallization from alcohol, m.p. 92-93°;

Phenylacetanilide with a yield of 0.36 g (88.5%), after recrystallization from alcohol, m.p. 116-117°;

Benzanilide with a yield of 0.55 g (88.9%), after recrystallization from alcohol, m.p. 161-162°;

p-Nitrobenzanilide with a yield of 0.55 g, after recrystallization from alcohol, m.p. 208-209°.

All the anilides were identified by the melting point of a mixed sample with the known pure substances.

SUMMARY

1. The reaction of p-nitrobenzoic acid with the trianilide, tri-p-toluidide and dianilide of phosphoric acid and with the trianilide, dianilide, triamide and monoamide of phenylsulfonimidophosphoric acid, was studied.

2. It was shown that only the trianilide of the phosphoric acid amides enumerated above appears to be a phenylamidating agent.

3. It was shown that the trianilide of phosphoric acid can be successfully employed for the direct phenylamidation of carboxylic acids of the fatty and aromatic series.

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* See Consultants Bureau Translation, page 233

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TRIBROMOPHOSPHAZOSULFONARYLS

A. V. Kirsanov and Yu. M. Zolotov

It has recently been found that trichlorophosphazosulfonaryls are formed in very excellent yields during the action of phosphorus trichloride on the sodium salts of the chloroamides of arylsulfonic acids [1]. It was of interest to investigate how general this reaction is and whether by using it, it is possible to obtain the hitherto unknown tribromophosphazosulfonaryls according to the formula:

$$ArSO_2NNaCl + PBr_3 \longrightarrow NaCl + ArSO_2N{=}PBR_3.$$

The experiments showed that the reaction of phosphorus tribromide with anhydrous sodium salts of chloroamides of arylsulfonic acids proceeds very readily, and tribromophosphazosulfonaryls are formed as the chief products, although not in such high yields as the trichlorophosphazosulfonaryls. If the reaction is conducted without solvent, then the yields do not exceed 50% of the theoretical, but if the reaction is conducted in a solution of carbon tetrachloride, then tribromophosphazosulfonaryls are formed in yields of 70-85% of the theoretical. The preparation of the tribromophosphazosulfonaryls is always accompanied by the formation of side products and the evolution of a small quantity of free bromine.

The tribromophosphazosulfonaryls are crystalline compounds, colorless or slightly colored with a light yellow color, and with a very faint peculiar odor. Tribromophosphazosulfonaryls are rather rapidly decomposed in moist air and readily react with water, amines, phenols and alcohols.

The tribromophosphazosulfonaryls are comparatively low-melting; they begin to soften on heating in a capillary a few degrees below the melting point and melt with decomposition, being converted into a reddish-brown liquid. The tribromophosphazosulfonaryls are readily soluble in acetone and benzene, and are difficultly soluble in ether and carbon tetrachloride.

EXPERIMENTAL

From 100 to 200 ml of dry carbon tetrachloride and 20 ml of a 1-M solution of phosphorus tribromide in carbon tetrachloride (270.7 g/liter) were added to 0.02 mole of carefully dried and powdered sodium salt of the chloroamide of the arylsulfonic acid. The mixture was energetically stirred for 10-15 minutes. At the same time an appreciable evolution of heat proceeded in the mixture, the residue of sodium salt gradually changed its appearance and the liquid became slightly yellowish. To complete the reaction, the mixture was boiled with a reflux condenser on a water bath for an hour. The reaction mixture became reddish-brown, which is to be explained by the evolution of a small quantity of free bromine. The boiling liquid was then quickly filtered, the residue was discarded, and the filtrate was left to crystallize. On cooling, the tribromophosphazosulfonaryls precipitated in the form of well-formed crystals. The product was drawn off, washed with carbon tetrachloride and dried in a vacuum-desiccator over paraffin and sulfuric acid. By evaporating down the mother liquor, some additional quantity of the product could be obtained. To purify the tribromophosphazosulfonaryls, they were recrystallized from carbon tetrachloride. During all the operations the reaction mixture and the solutions as much as possible should be protected from the action of the moisture of the air. To obtain good yields, the sodium salts of the chloroamides of arylsulfonic acids should be carefully dehydrated. According to the literature data, these salts detonate on heating to the melting point (150-200°). Actually, the sodium salts of the chloroamides detonate with remarkable force on drying in a vacuum at even 80°. It is consequently better to dry these salts at room temperature in a vacuum-desiccator initially over sulfuric acid and then over phosphorus pentoxide, to constant weight, which requires about four days.

In this manner the following were obtained:

Tribromophosphazosulfonophenyl, $C_6H_5SO_2N{=}PBr_3$ yield 6.1 g (71.6%), m.p. 94-97° (uncorr.), crystallized from carbon tetrachloride in the form of fine prisms.

0.2798 g substance: 0.3736 g AgBr; 16.2 ml 0.2046 N NaOH. 0.2858 g substance: 0.3768 g AgBr; 16.5 ml 0.2046 N NaOH. Found: % Br 56.82, 56.11; equivalents of acid during hydrolysis 5.04, 5.02. $C_6H_5SO_2NPBr_3$. Calculated: % Br 56.31; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-o-tolyl, $o\text{-}CH_3C_6H_4SO_2N{=}PBr_3$, yield 7.52 g (85.4%), m.p. 148-151° (uncorr.); softened at 144°, crystallized from carbon tetrachloride in the form of long needles.

0.2875 g substance: 0.3681 g AgBr; 15.8 ml 0.2046 N NaOH. 0.2618 g substance: 0.3345 g AgBr; 14.5 ml 0.2046 N NaOH. Found: % Br 54.48, 54.37; equivalents of acid during hydrolysis 4.94, 4.98. $C_7H_7SO_2NPBr_3$. Calculated: % Br 54.49; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-p-tolyl, $CH_3C_6H_4SO_2N{=}PBr_3$, yield 6.86 g (79.0%), m.p. 138-141° (uncorr.), softened at 132°, crystallized from carbon tetrachloride in the form of fine prisms.

0.2176 g substance: 0.2814 g AgBr; 12.0 ml 0.2046 N NaOH. 0.3460 g substance: 0.4602 g AgBr; 19.1 ml 0.2046 N NaOH. Found: % Br 55.03, 54.28; equivalents of acid during hydrolysis 4.96, 4.96. $C_7H_7SO_2NPBr_3$. Calculated: % Br 54.49; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-α-naphthyl, $\alpha\text{-}C_{10}H_7SO_2N{=}PBr_3$, yield 6.78 g (70.5%), m.p. 157-159° (uncorr.), softened at 152°, crystallized from carbon tetrachloride in the form of coarse prisms.

0.3238 g substance: 0.3824 g AgBr; 16.4 ml 0.2046 N NaOH. 0.2526 g substance: 0.3008 g AgBr; 12.9 ml 0.2046 N. NaOH. Found: % Br 50.25, 50.67; equivalents of acid during hydrolysis 4.93, 4.97. $C_{10}H_7SO_2NPBr_3$. Calculated: % 50.37; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-β-naphthyl, $\beta\text{-}C_{10}H_7SO_2N{=}PBr_3$, yield 6.32 g (66.1%), m.p. 150-153° (uncorr.), softened at 146°, crystallized from carbon tetrachloride in the form of fine prisms.

0.2342 g substance: 0.2780 g AgBr; 12.1 ml 0.2046N. NaOH. 0.2608 g substance: 0.3082 g AgBr; 13.4 ml 0.2046 N. NaOH. Found: % Br 50.51, 50.29; equivalents of acid during hydrolysis 5.03, 5.00. $C_{10}H_7SO_2NPBr_3$. Calculated: % Br 50.37; equivalents of acid during hydrolysis 5.00

SUMMARY

1. It was shown that tribromophosphazosulfonaryls are obtained in excellent yields by the action of the sodium salts of the chloramides of aromatic sulfonic acids on phosphorus tribromide.

2. Tribromophosphazosulfonophenyl, o-tolyl, p-tolyl, α-naphthyl and β-naphthyl were prepared and described.

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THE REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

VI. ESTERS OF α-HYDROXYPROPYLPHOSPHINIC ACID

V. S. Abramov and N. A. Ilyina

We have shown [1] that aldehydes and ketones react with dialkylphosphorous acids and yield addition products at the carbonyl group. The reaction is of interest on account of the fact that the dialkylphosphorous acids along with a few other acids as, for example, hydrocyanic and sulfurous acids, yield stable compounds which are often crystalline substances. In connection with this, the reaction can be considered to be characteristic of the carbonyl group. The addition of dialkylphosphorous acids to the carbonyl group proceeds in the presence of catalysts, which function can be performed by the alcoholates of the alkaline metals. The reaction proceeds rapidly with the evolution of heat, and, as we represented it, the dialkylphosphorous acids react in the enol form. A scheme was proposed to explain the mechanism of the course of the reaction of dialkylphosphorous acids with carbonyl compounds [2].

The completeness of the reaction depends on the radicals of the carbonyl group. The reaction proceeds better and more completely with aldehydes than with ketones, and, moreover, if the entering radicals increase the polarization of the carbonyl groups, then the reaction also proceeds better and more completely. The indicated rules were verified for a whole series of examples.

Investigations of the preparation and study of the properties of esters of α-hydroxypropylphosphinic acids are described in the present article. Esters of α-hydroxypropylphosphinic acid were obtained by the action of propionaldehyde on various dialkylphosphorous acids. Freshly prepared saturated solution of sodium methylate served as the catalyst for the reaction. The duration of the reaction of the dialkylphosphorous acids with propionaldehyde and the physical properties of the esters of α-hydroxypropylphosphinic acids obtained are set forth in the table.

In considering the data of the table it is first of all evident that the increase in the temperature of the reaction mass is the greater the larger the hydrocarbon radical of the dialkylphosphorous acid. In addition, less catalyst (sodium methylate) is required, the larger the hydrocarbon radical of the dialkylphosphorous acid. A manifold influx of catalyst is required to effect the reciprocal reaction of propionaldehyde with dimethylphosphorous acid, and a total of about 1 ml of it was consumed, while the reaction with dibutyl and diisobutylphosphorous acid proceeds with one or two drops of sodium methylate solution.

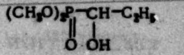
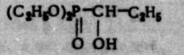
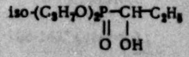
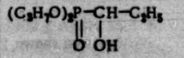
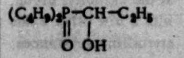
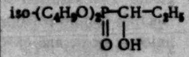
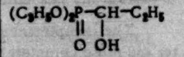
The course of the reaction controls the completeness in the yield of the ester of α-hydroxypropylphosphinic acid. The yield of esters is increased with increasing size of the hydrocarbon radical of the dialkylphosphorous acid, but it is necessary to keep in sight in this connection that with increasing size of the ester molecule partial decomposition occurs during distillation; for example, during that of the dibutyl ester of α-hydroxypropylphosphinic acid. The decomposition of esters of α-hydroxyalkylphosphinic acids during heating (distillation) was established previously by us [3].

We determined the purity of the product and the completeness of the reaction by measuring the refractive index. The refractive index of the reaction mixture after reaction is the closer to the coefficient of pure ester of α-hydroxypropylphosphinic acid, the larger the hydrocarbon radical of the dialkylphosphorous acid.

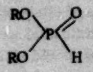
To generalize all that has been said, it can be stated that the reactivity of dialkylphosphorous acids in reactions with carbonyl compounds is the greater, the larger the hydrocarbon radical of the dialkylphosphorous acid.

Such a conclusion contradicts the generally accepted point of view. It is ordinarily considered that substances are the more reactive the smaller the radicals of which they are composed. Such a conclusion (at first glance conflicting) can be explained. According to the investigations of A. E. Arbuzov [4], dialkylphosphorous acids occur

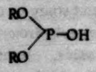
Reaction between Dialkylphosphorous Acids and Propionaldehyde and Constants of the

Dialkylphosphorous acid	Quantity of reacting substances (in g)		Increase in temperature (in °C)	n_D^{20} before distillation	Esters obtained
	Acid	Propionaldehyde			
$(CH_3O)_2POH$	11.0	5.8	23-69	1.4183	 $(CH_3O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
$(C_2H_5O)_2POH$	13.8	5.8	24-88	1.4232	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
iso-$(C_3H_7O)_2POH$	12.5	4.5	24-76	1.4180	 iso-$(C_3H_7O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
$(C_3H_7O)_2POH$	12.5	4.5	23-106	1.4343	 $(C_3H_7O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
$(C_4H_9O)_2POH$	14.4	4.5	25-102	1.4382	 $(C_4H_9)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
iso-$(C_4H_9O)_2POH$	14.4	4.5	25-122	1.4350	 iso-$(C_4H_9O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$
$(C_3H_5O)_2POH$	12.2	4.5	24-100	1.4530	 $(C_3H_5O)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{\vert}}{CH}-C_2H_5$

in two tautomeric forms, in one of which the phosphorus is pentavalent (I) and in the other, travalent (II):



(I)



(II)

It is, however, impossible to separate these two forms due to their tautomeric interconversion. A. E. Arbuzov, M. I. Batuev and V. S. Vinogradova [5] offered a preliminary communication concerning the results of an investigation of the structure of dialkyl phosphorous acids by the method of Raman spectra which demonstrated that a broad, intense line is observed in the dialkylphosphorous acids which corresponds to the valence vibration frequency of P—H. This dialkylphosphorous P—H group is subjected to a strong molecular influence in the form of a hydrogen bond of the P—H. . .P or P—H. . .O type. In addition, the valence vibrations of P=O are observed in the spectra of the dialkylphosphorous acids which also have a diffuse character. Thus, in the liquid state the dialkylphosphorous acids have a pronounced pentavalent phosphorus structure (I). If, in addition to the form (I) there were also the form (II) in the dialkylphosphorous acids, it would lead to the appearance of the frequencies of the O—H group in the Raman spectra of the acids. In the spectra of dipropyl- and dibutylphosphorous acids there is actually detected a narrow band with the O—H valence vibration frequency. The intensity of the O—H band is comparatively small and is masked by intermolecular influences of the hydrogen bond type. Thus, in liquid dialkylphosphorous acids, the form (II) is also present along with form (I) in the propyl and butylphosphorous acids.

As we have already said, the reaction of aldehydes and ketones with dialkylphosphorous acids proceeds in the enol form, i.e., form (II). The greater the possibility of ready formation of form (II), the more readily and intensively the reaction with aldkehydes and ketones should proceed. A similar pattern was also observed by us during the preparation of esters of α-hydroxypropylphosphinic acids: the conclusion which we previously reached, consequently can be formulated as folows: the reactivity of dialkylphosphorous acids with carbonyl compounds is the greater, the greater the possibility of forming their enol forms. Thus, the pattern for the reaction of dialkylphosphorous acids with propionaldehyde which we established is found to be in complete agreement with the investigations of A. E. Arbuzov relative to the structure of dialkylphosphorous acids by the Raman spectra method. The conclusions reached concerning the pattern of the course of the reactions of dialkylphosphorous acids with propionaldehyde were also confirmed for reactions with tetrahydrobenzaldehyde.

Esters of α-Hydroxypropylphosphinic Acids Obtained

Boiling point (in °)	d_4^{20}	n_D^{20} after distillation	MR_D		Phosphorus content (in %)		Yield of ester (in %)
			calculated	found	calculated	found	
116-117 (1 mm)	1.1834	1.4413	37.17	37.48	18.45	18.70, 18.73	25.83
120-121 (1.5 mm)	1.0955	1.4360	46.40	46.78	15.81	15.88, 15.65	52.5
112-113 (2 mm)	1.0299	1.4295	55.64	56.01	13.83	13.91, 13.65	48.0
126-128 (1 mm)	1.0454	1.4365	55.64	56.08	13.83	13.84, 14.05	30.6
130-132 (1 mm)	1.0241	1.4382	64.88	64.62	12.30	11.75, 12.05	43.4
139-140 (2 mm)	1.0150	1.4378	64.88	65.11	12.30	12.25, 12.46	71.5
129-130 (1 mm)	1.0961	1.4600	54.78	54.98	14.09	13.96, 13.91	49.4

EXPERIMENTAL

Reaction of Dialkylphosphorous Acids with Propionaldehyde

An equimolecular mixture of dialkylphosphorous acid and propionaldehyde was carefully stirred, the temperature measured, and the catalyst – a freshly prepared saturated solution of sodium methylate – added dropwise it; an increase in the temperature was observed. Subsequent portions of sodium methylate were poured in only when the temperature of the mixture began to fall. Introduction of the catalyst was ceased when addition of the next portion did not give an increase in the temperature. Upon completion of the reaction the products were distilled. The course of the reaction and the physical constants of the esters obtained are set forth in the table.

It was ordinarily possible to limit ourselves to one vacuum distillation to obtain analytically pure esters. The methyl, ethyl and allyl esters were exceptions.

SUMMARY

1. The action of dialkylphosphorous acids on propionaldehyde was studied and 7 new esters of α-hydroxypropylphosphinic acids were obtained, the structure and constants of which are set forth in the table.

2. It was established as a result of the investigation that the reaction of dialkylphosphorous acids with carbonyl compounds proceeds the more readily and completely, the larger the hydrocarbon radical of the acid. This conclusion is found to be in full agreement with the conclusions concerning the structure of the dialkylphosphorous acids formed by studying them with the Raman spectra method.

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* See Consultants Bureau Translation, page 709.

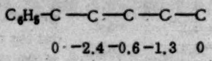
PARACHORS OF CERTAIN ESTERS OF ETHYLENEGLYCOLARSENIOUS ACID

Gilm Kamai and K. I. Kuzmin

It has been shown in a number of works which have recently appeared [1, 2], that investigation of the parachors of organic compounds permits certain particulars of the fine structure of organic compounds to be established.

Conclusions concerning one or another particular of the fine structure are made on the basis of comparison of the experimentally found parachors with those calculated from the group values and the corresponding corrections, taking account of the interaction of atoms not directly bound to each other in various structural variations. This method has been successfully applied for the study of the structure of various compounds with long hydrocarbon chains. Up to the present time, little attention has been paid to the study of the structure of cyclic compounds with long side chains.

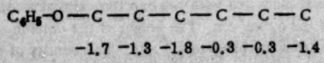
Gibbling [3] considers that in alkylbenzenes the side chain is deflected in the direction of the aromatic ring under the influence of polar molecules. This requires the introduction of a correction for the deflection for the first three members of the chain, after which the normal magnitude of the standard value of the CH_2 group, equal to 39.8 is reached. The corrections for the deflection of the chain according to the data of Gibbling, amout to:



$$C_6H_5\!-\!\underset{0}{C}-\underset{-2.4}{C}-\underset{-0.6}{C}-\underset{-1.3}{C}-\underset{0}{C}$$

It should be noted, however, that the calculations of Gibbling were based on a very small amount of experimental data and as a consequence of that, are not entirely accurate.

There is information in the literature concerning the parachors of cyclic compounds with longer side chains. We have calculated from the data of Vogel [4] that for the side chains of phenol ethers it is necessary to introduce the following corrections:

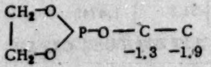


$$C_6H_5\!-\!O-\underset{-1.7}{C}-\underset{-1.3}{C}-\underset{-1.8}{C}-\underset{-0.3}{C}-\underset{-0.3}{C}-\underset{-1.4}{C}$$

It follows from the parachors of methylcyclohexane [5], octylcyclohexane [6] and octadecylcyclohexane [6] that the average difference of the standard values applying to one CH_2 group of the side chain, ΔCH_2 amounts to: for the range from methylcyclohexane to octylcyclohexane $\Delta CH_2 = 39.4$, and for the range from methylcyclohexane to octadecylcyclohexane $\Delta CH_2 = 39.8$.

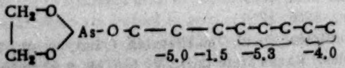
Thus, the corrections for the side chain of cyclic paraffins are considerably less than the corrections for ethers of phenol and alkylbenzenes.

In 1950 B. A. Arbuzov and V. S. Vinogradova [7] initiated a study of the parachors of cyclic esters of inorganic acids. They studied the parachors of the cyclic esters of carbonic, sulfurous and phosphorous acids. B. A. Arbuzov and V. S. Vinogradova employed the following corrections for the interaction of the side ester chain with the ring in the cyclic esters of phosphorous acid:



We have studied the parachors of certain esters of ethyleneglycolarsenious acid.* The data obtained are presented in Table 1.

Corrections for the interaction of the side ester chain with the ring calculated from the data of Table 1, amount to:



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* The esters of ethyleneglycolarsenious acid were synthesized by Z. L. Khisamova.

TABLE 1

Ester	Observed parachor	C. E.*	S. V.**
Methyl	254.7	0.7	254.0
Ethyl	289.2	0.8	288.4
Propyl	327.7	1.0	326.7
Hexyl	432.1	1.8	430.3
Octyl	504.3	2.5	501.8

on the average for each group.

The observed magnitudes of the corrections are considerably different from the corresponding corrections for the esters of ethyleneglycolphosphorous acid and phenol ethers. In all probability, the nature of the atoms forming the ring exerts a strong influence on the magnitude of the corrections for the side chain.

The deviation of the standard value for the CH_2 group (from the normal quantity observed even in CH_2 groups very far removed from the ring) in the phenol ethers and in the esters of ethyleneglycolarsenious acid leads us to think that there are apparently some specific structural peculiarities in the molecules of cyclic compounds with a side chain which depend on the presence of the ring. The character of these peculiarities has not been exposed up to the present time.

The study of the parachors of the esters of ethyleneglycolarsenious acid demonstrated that the parachors found experimentally are in excellent agreement with those calculated theoretically, with the application of a twofold correction for parallelism for each CH_2 group, i.e., $-2 \cdot 2.2$. The calculated data are set forth in Table 2.

TABLE 2

Ester	S. V.	C. E.	Parachor		Discrepancy (in %)	Corrections
			calculated	found		
Methyl	254.0	0.7	254.7	254.7	0	–
Ethyl	289.0	0.8	289.8	289.2	+ 0.2	−4.4
Propyl	324.4	1.0	325.4	326.7	−0.4	−8.8
Hexyl	430.6	1.8	432.4	432.1	+ 0.1	−22.0
Octyl	501.4	2.5	503.9	504.3	−0.1	−30.4

What causes the necessity of such a correction has not yet been successfully established. Thus, the question of the structure of the esters of ethyleneglycolarsenious acid can not be considered resolved at the present time. A considerably greater amount of experimental data is required for the conclusive elucidation of the peculiarities of the structure of cyclic compounds with long side chains.

EXPERIMENTAL

Before the determination of the surface tension, the density and the refractive index, all the substances were subjected to vacuum distillation. The surface tension was determined by the maximum bubble pressure method. The surface tension of each substance was measured with two capillary tips at a temperature of 20° ± 0.1°. The discrepancy between the results did not exceed 0.2 dynes/cm. The height of the column of manometric liquid was measured with a microcathetometer with an accuracy of up to 0.1 mm. The density of the substances under investigation was measured with an ordinary pycnometer with a volume of about 3 ml with a capillary neck. The refractive indices were determined on an Abbe refractometer. The physical constants of the esters of ethyleneglycolarsenious acid which were investigated are summarized in Table 3.

TABLE 3

Ester	Boiling point (in °)	d_0^{20}	γ_{20}	n_D^{20}
Methyl	51-53 (11 mm)	1.5824	34.8	1.4850
Ethyl	60-62 (11 mm)	1.4723	31.3	1.4788
Propyl	74-75 (12 mm)	1.3949	30.8	1.4760
Hexyl	127.5-129.5 (18 mm)	1.2924	31.3	1.4752
Octyl	123.5-124 (4.5 mm)	1.2389	31.2	1.4748

SUMMARY

1. The parachors of five esters of ethyleneglycolarsenious acid were determined.

2. The problem concerning the structure of the esters of ethyleneglycolarsenious acid and also of other cyclic compounds with long side chains can not be considered solved at the present time.

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* Correction for expansion.

** Standard value.

INVESTIGATIONS IN THE FIELD OF QUINOLINE DERIVATIVES

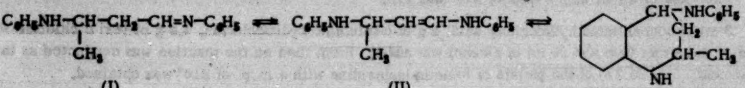
X. SYNTHESES OF QUINOLINES FROM DIETHYLIDENEARYLAMINES

B. I. Ardashev

The mechanism of decomposition of ethylidenarylamine dimers, i.e., the so-called Eibner and Eckstein bases, is directly involved in the formation of quinaldine and its derivatives. Miller considered that it was impossible to obtain more than 22% quinaldine from the dimer of ethylidenaniline [1]. N. S. Kozlov demonstrated in a number of cases that during the formation of quinaldine and its derivatives from aromatic amines and acetylene in neutral medium, dimers of ethylidenarylamines arise [2-6], from which he obtained quinaldine and its derivatives.

To solve the problem of the mechanism of formation of quinolinic bases from diethylidenarylamines it is necessary to know their structure. Eibner considered that the ethylidenaniline dimers were cis and trans isomers of the fumaric and maleic acid type [7]. Later the possibility of tautomerism of bases of the type of the anil of β-anilinobutyraldehyde (I) and diethylidenaniline (II) [8, 9, 10] was demonstrated. In 1951 Zalukaev specified the structure of diethylidenaniline as 2-methyl-4-anilino-1,2,3,4-tetrahydroquinaldine (III) [11, 12].

Thus, the dimers of ethylidenaniline can exist in the form of several tautomers, of which the more stable is the cyclic form:



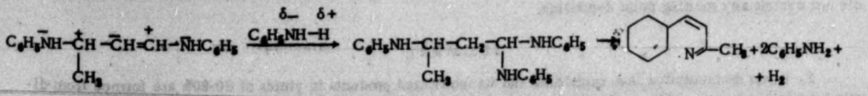
(I) (II) (III)

Upon heating, particularly in acidic medium, the cyclic form is decomposed and is readily converted into quinaldine and aniline with the evolution of hydrogen.

Although the hypothesis has sometimes been expressed that diethylidenarylamines are formed in a Debner-Miller reaction, up to the present time their decomposition has been effected only in a neutral medium or thermally. In spite of this, Zalukaev [11] reported the preparation by him of quinaldine from diethylidenaniline with a yield of 51% of the theoretical; under the conditions of his experiment in neutral medium, however, it was impossible to achieve a yield greater than 25-30%. Correct calculation from his numerical data leads to a magnitude of the yield of 27% [11].

The experiments set up by us for the preparation of quinaldine and its derivatives from the hydrochlorides of diethylidenarylamines lead to a yield of 80-93% of the theoretical.

The catalytic action of aniline hydrochloride was established; it was demonstrated that the maximum yield of quinaldine and its derivatives is obtained with equimolar quantities of the amine salt and the base. In accordance with this, the mechanism of decomposition of the ethylidenaniline dimer in the presence of aniline should be represented in the following manner:



Extreme conditions are not required during the addition of aniline for the decomposition of the base; the reaction can be effected in alcoholic solution with the use of ferric chloride as oxidizing agent. The yield of quinaldine is about 80% of the theoretical. The syntheses from diethylidenarylamines find preparative application for the preparation of several quinolinic bases which are formed in small yields by other methods, for example, 8-toluquinaldine, nitroquinaldines and others. From the corresponding ethylidenaniline dimers 8-toluquinaldine is obtained with a yield of 87%, 6-nitroquinaldine with a yield of 90%.

The investigation conducted has significance for the study of the mechanism of quinaldinic syntheses and, in particular, the mechanism of the Debner-Miller reaction.

EXPERIMENTAL

The dimer of ethylidenaline (trans) was obtained by the method described previously [11]. The yield of the dimer with a m.p. of 117° was 87%.

Synthesis of Quinaldine

Experiment 1. A mixture of 3 ml of concentrated hydrochloric acid and 3 ml of water was poured over 3 g of the dimer base, and 1.5 g of aniline hydrochloride was added and the resulting mixture then heated with a reflux condenser on a boiling water bath for 3 hours. After rendering the solution alkaline with sodium hydroxide, and steam distilling, the quinaldine was precipitated from the distillate in the form of the picrate by a saturated solution of picric acid. The picrate was filtered off, washed with alcohol to remove the excess picric acid and the aniline which partially was adsorbed by the picrate, dried, weighed and the melting point determined. 3.75 g (80%) of quinaldine picrate with a m.p. of 190° was obtained.

No melting point depression was observed in a mixed sample with known quinaldine picrate.

Experiment 2. 1.3 g of aniline hydrochloride and 3.2 g of ferric chloride were added to 2.6 g of the hydrochloride of the dimer base, and 20 ml of alcohol added. The mixture was heated for 3 hours on a boiling water bath with a reflux water condenser and the picrate was isolated as described in the first experiment. 2.2 g (73.3%) of quinaldine picrate with a m.p. of 191° was obtained.

Synthesis of 8-Methylquinaldine

The dimer of ethylidene-o-toluidine (trans) was obtained analogously to the dimer of ethylidenaniline by letting a mixture stand for a week.

The yield of dimer with a m.p. of 115° was 97%.

3 ml of concentrated hydrochloric acid, 2 g of o-toluidine hydrochloride, 4.8 g of ferric chloride were added to 4 g of the dimer base and 20 ml of alcohol was added. From then on the reaction was conducted as in the second experiment. 5 g (86.2%) of the picrate of 8-methylquinaldine with a m.p. of 210° was obtained.

Synthesis of 6-Nitroquinaldine

13.8 g of p-nitroaniline was dissolved in a mixture of 150 ml of alcohol and 100 ml of water to obtain the dimer of 6-nitroethylideneaniline, and 7 ml of freshly prepared acetaldehyde was then added. After heating for 30 mintues with a reflux condenser on a water bath at 70-80°, a precipitate settled out that was initially of an orange color, but which quickly reddened on further heating. The total length of the heating was 1.5 hours, the last 0.5 hour of the heating was carried out on the boiling water bath. The precipitate was filtered off and washed several times with hot water to remove unreacted p-nitroaniline. After drying, 4.5 g of a flocculent powder of a dark brick-red color with a m.p. of 197° was obtained. Since it consisted of a mixture of the cis and trans bases [4], the melting point varied in different experiments within a range of 20°.

The yield amounted to 91.8%, calculated on the basis of the p-nitroaniline taken for the reaction.

10 g of the dimer base was mixed with 5 g of p-nitroaniline, 20 ml of dilute hydrochloric acid (1: 1) was added and the mixture was heated with a reflux condenser on a water bath for 3 hours. After cooling the reaction mixture which had been diluted with water, a precipitate settled out, consisting chiefly of p-nitroaniline and an insignificant quantity of admixture of polymerization products. The filtrate was rendered alkaline and 6-nitroquinaldine in a quantity of about 8 g was isolated from it. The 6-nitroquinaldine was recrystallized from hot water; 5.15 g (90%) of product with a m.p. of 170° was obtained. A mixed sample with what was known to be the well-known p-nitroquinaldine did not exhibit any melting point depression.

SUMMARY

1. It was demonstrated that quinaldine and its substituted products in yields of 80-90% are formed from diethylidenarylamines in acidic medium and also in alcoholic solution in the presence of the oxidizing agent ferric chloride.

2. The new method of synthesizing quinolines from diethylidenarylamines can be recommended as a preparative method for obtaining derivatives of quinaldine from o-substituted amines, from nitroamines and for the synthesis of various quinaldine derivatives obtained in poor yields by other methods.

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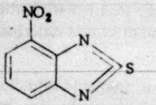
SYNTHESIS OF PIAZOTHIOLE(3,4-BENZO-1,2,5-THIODIAZOLE) AND ITS DERIVATIVES. II.

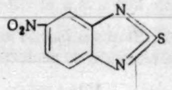
A. M. Khaletsky and V. G. Pesin

In the preceding article [1] we described the synthesis of piazothiole and its nitro-, amino- and acylamino derivatives. In connection with the investigations of Efros and Levit [2], it is of interest to supplement the material of our preceding work with data which we have with respect to the synthesis and investigation of 2-nitro- and 2-amino piazothiole having compared them with the data of the indicated authors.

Efros and Levit indicate that during the nitration of piazothiole they obtained 1-nitropiazothiole(I); as regards 2-nitropiazothiole(II), they confirmed that in agreement with the electronic representation developed by them with respect to disturbance of the alignment of the bonds in the benzene ring, the latter (II) can not be obtained by the reaction of 4-nitro-1,2-diaminobenzene with thionyl chloride.

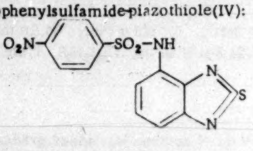


(I)

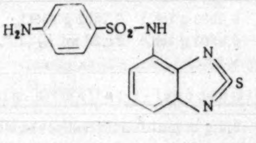


(II)

We have demonstrated that 2-nitropiazothiole is formed during the reaction of 4-nitro-1,2-diaminobenzene with thionyl chloride, and that 2-nitropiazothiole when reduced with iron in presence of 1-4% acetic acid is converted into 2-aminopiazothiole. Consequently, the assertion of the authors that 4-nitro-1,2-diaminobenzene does not enter into reaction with thionyl chloride, appears to be erroneous. At the same time it should be noted that it follows from the syntheses of derivatives of aminopiazothiole conducted by us that during the nitration of piazothiole the nitro group replaces the hydrogen of the benzene ring in position 1. Thus, during the condensation of aminopiazothiole obtained from nitropiazothiole (the product of the nitration of piazothiole) with the sulfochloride of p-nitrobenzene, p-nitrophenylsulfamide piazothiole (III) is formed which, upon reduction with sodium sulfide is converted into the corresponding p-aminophenylsulfamide-piazothiole(IV):

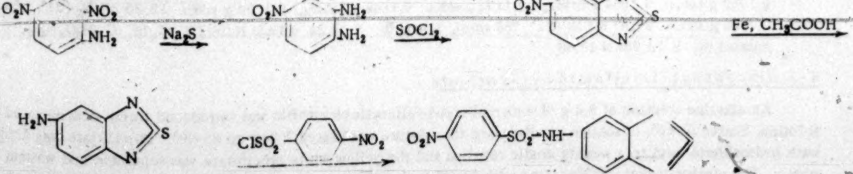


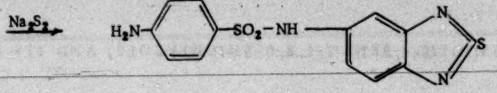
(III)



(IV)

The structure of the sulfamides set forth was confirmed by the synthesis of their isomeric compounds on the basis of the following reactions:





It follows from what has been set forth that with respect to the theory of substitutions in the benzene ring, nitro- and aminopiazothiokes can exist in the form of two isomers.

EXPERIMENTAL

2-Nitropiazothiole

15.3 g of 1-nitro-3,4-diaminobenzene and 34 g of thionyl chloride (40% excess) were heated with 75 ml of dry toluene while being stirred for 8 hours. The dark colored reaction mixture was cooled and poured into 0.5 kg of a mixture of ice and water. After the liquid layers (toluene and aqueous) had clarified, they were poured into a separatory funnel and the aqueous layer was separated from the toluene layer. The latter along with the crystalline mass was steam distilled. After distilling off the bulk of the toluene together with which an insignificant quantity of 2-nitropiazothiole was extracted, the latter distilled over in the form of almost colorless crystals. 3.3 g (18.2%) of 2-nitropiazothiole with a m.p. of 127-128° was obtained.

2-Nitropiazothiole was slightly soluble in boiling ethyl alcohol, insoluble in methyl alcohol and soluble in acetone and carbon tetrachloride on heating. It crystallized from the latter in the form of colorless clusters.

0.1001 g sub.: 0.1265 g $BaSO_4$. 0.1039 g sub.: 0.1352 g $BaSO_4$. 0.1793 g sub.: 35.53 ml N_2 (17°, 760 mm). 0.1645 g sub.: 33.63 ml N_2 (18°, 756 mm). Found %: S 17.33, 17.87; N 22.95, 23.31. $C_6H_3O_2N_3S$. Calculated %: S 17.68; N 23.20.

2-Aminopiazothiole

A mixture of 6 g of 2-nitropiazothiole, 18 g of iron filings, 100 ml of water and 4 g of acetic acid was heated while being stirred for 0.5 hour to 100°. The cooled mixture was rendered alkaline with sodium carbonate and separated from the iron sludge. The filtrate and the iron sludge were extracted with ether and poured into a crystallizing pan. After driving off the ether 3.1 g of a substance melting at 103-111° was obtained; after recrystallization from hot water, 2.4 g (48%) of crystals with a m.p. of 114° was isolated.

2-Aminopiazothiole dissolves in hot water and many organic solvents; its solubility in hot water is considerably greater than that of 1-aminopiazothiole.

0.0986 g sub.: 0.1552 g $BaSO_4$. 0.1133 g sub.: 0.1726 g $BaSO_4$. 0.1428 g sub.: 34.60 ml N_2 (19°, 756 mm). 0.0908 g sub.: 21.38 ml N_2 (17°, 764 mm). Found %: S 21.64; N 27.34. $C_6H_5N_3S$. Calculated %: S 21.19; N 27.81.

4-Nitrophenyl-1-sulfamide-piazothiole

8.2 g of p-nitrobenzosulfochloride [3] in a mixture with 10 ml of acetone was added gradually to a solution, heated to 50°, of 5 g of 1-aminopiazothiole in 15 ml of pyridine. The mixture was heated 1 hour to 60°, cooled, diluted with water and acidified with hydrochloric acid. The precipitate was filtered off and dissolved in a 4% solution of sodium hydroxide. The filtrate was precipitated with hydrochloric acid, and the precipitate after separation and washing with water was dried at 100°. 8.4 g (75%) of a crystalline substance with a m.p. of 163-164° was obtained.

0.1059 g sub.: 0.1054 g $BaSO_4$. 0.1172 g sub.: 0.1642 g $BaSO_4$. 0.1054 g sub.: 15.35 ml N_2 (21°, 756 ml). 0.1856 g sub.: 27.97 ml N_2 (21°, 756 mm). Found %: S 19.24, 19.45; N 16.19, 16.76. $C_{12}H_8O_4N_4S_2$. Calculated %: S 19.05; N 16.66.

4-Aminophenyl-1-sulfamide piazothiole

An alkaline solution of 8.4 g of 4-nitrophenyl-1-sulfamide-piazothiole was introduced into a concentrated aqueous solution, heated to 60°, of sodium disulfide and the mixture was heated 1 hour to 65-70°. The filtrate was acidified with hydrochloric acid to a weakly acidic reaction and the yellow-white precipitate was separated and washed with water. The mother liquor was extracted with hot 3% hydrochloric acid, cooled with ice, and the hydrochloride which separated was filtered off. The residue after extraction consisted of a mixture of sulfur with a small quantity of unreacted nitrocompound. The compounds of the fraction were dissolved in a dilute solution of sodium hydroxide, the solution was treated with animal carbon and the filtrate was again precipitated with hydrochloric acid. The 4-aminophenyl-1-sulfamide-piazothiole which separated out was removed, washed with water and dried at 100°. 5 g (67%) of a crystalline substance with a m.p. of 193-194° was obtained.

0.1118 g sub.: 0.1723 g $BaSO_4$. 0.1068 g sub.: 0.1631 g $BaSO_4$. 0.1531 g sub.: 24.60 ml N_2 (19°, 737 mm). 0.1373 g sub.: 22.36 ml N_2 (20.5°, 737 mm). Found %: S 21.51, 21.15; N 17.81, 17.9. $C_{12}H_{10}O_2N_4S_2$. Calculated %: S 20.91; N 18.30.

4-Nitrophenyl-2-sulfamide piazothiole

The condensation of 2-aminopiazothiole with p-nitrobenzosulfochloride was conducted analogously to its isomer, m.p. 198-200°; yield 77%.

0.1713 g sub.: 0.2473 g $BaSO_4$. 0.1657 g sub.: 0.2278 g $BaSO_4$. 0.1063 g sub.: 16.08 ml N_2 (18°, 732 mm). 0.1253 g sub.: 18.32 ml N_2 (22°, 752.5 mm). Found %: S 19.54, 18.77; N 17.10, 16.74. $C_{12}H_8O_4N_4S_2$. Calculated %: S 19.05; N 16.66.

4-Aminophenyl-2-sulfamide piazothiole

The sulfamide was obtained by reduction of 4-nitrophenyl-2-sulfamide-piazothiole under conditions analogous to the synthesis of its isomer. The extraction of the raw reduction product was conducted with 10% hydrochloric acid; m.p. 245-250°; yield 63%.

0.1281 g sub.: 0.1951 g $BaSO_4$. 0.1133 g sub.: 0.1745 g $BaSO_4$. 0.1608 g sub.: 27.08 ml N_2 (16°, 714 mm). 0.1504 g sub.: 25.0 ml N_2 (16°, 714 mm). Found %: S 21.36, 21.42; N 18.69, 18.54. $C_{12}H_{10}O_2N_4S_2$. Calculated %: S 20.91; N 18.30.

SUMMARY

1. It was found that during the nitration of piazothiole the nitro group replaces the hydrogen of the benzene ring in position 1.

2. The following were synthesized: 2-nitro- and 2-aminopiazothiole, 4-nitrophenyl-1-sulfamidepiazothiole, 4-aminophenyl-1-sulfamide piazothiole, 4-nitrophenyl-2-sulfamidepiazothiole and 4-aminophenyl-2-sulfamide-piazothiole.

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* See Consultants Bureau Translation, page 1981.

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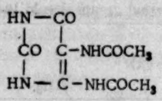
THE CONVERSION OF URIC ACID INTO 8-METHYLXANTHINE

I. STRUCTURE OF THE INTERMEDIATE SUBSTANCE

E. S. Golovchinskaya

The conversion of uric acid into 8-methylxanthine by means of its prolonged heating with acetic anhydride was described for the first time in a patent of the Beringer firm [1] at the beginning of the present century. At that time it was already known that this reaction proceeds in two phases and a hypothesis, concerning the mechanism of the reaction was first proposed [2]. After brief heating of uric acid with acetic anhydride an intermediate substance was successfully isolated which differed from the final 8-methylxanthine in a considerably greater solubility in water. The structure of 4-5-di-(acetylamino)-uracil (I) was then ascribed to it:

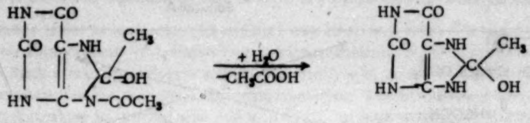


(I)

It was detected that during treatment with alkali only one of its acetyl groups was hydrolyzed. The compound $C_6H_8O_3N_4$ obtained as a result of the hydrolysis was considered as a monoacetyl derivative of 4,5-diaminouracil.

The first detailed investigation of the question of the structure of the intermediate substance was published in 1923 by Biltz and Schmidt [3]. These authors came to the conclusion that the intermediate substance consisted of a bicyclic carbinol (IIa), and not of the 4,5-di-(acetylamino)-uracil (I), as had been previously postulated.

They correspondingly ascribed to that substance obtained from it as a result of the saponification of one acetyl group, the structure (III):



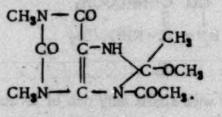
(IIa) (III)

As one of the basic arguments in favor of the carbinol structure of the intermediate substance, Biltz and Schmidt directed their attention to the fact that not only under the action of alkali, but under other saponification conditions as well, the hydrolysis of only one acetyl group occurred. The formation of the closed compound (IIa) was, in their opinion, the result of secondary cyclization, proceeding at the expense of the carbonyl carbon of the second "unsaponified" acetyl group. The only conflict with their assumption concerning a bicyclic structure (IIa) and (III) the authors found in the fact that the characteristic reactions for the hydroxyl group are absent in these substances. They explained this conflict by the position of the hydroxyl group in the molecule and the influence on it of neighboring groupings.

The disputable structure of the intermediate substance has served as the subject of the present investigation. It was begun with the study of its methylation with dimethyl sulfate in an aqueous-alkaline medium. By employing 2 moles of dimethyl sulfate and a pH of 7-8, a crystalline substance (VI) was obtained with a m.p. of 208-209°, which was soluble in alkalis separated from the solutions when they were acidified. According to the analysis it contained two methyl groups which, as was shown by its further conversion into 8-methyltheophylline [4], are bound to the nitrogen of the pyridine portion of the molecule. Its direct yield did not exceed 20%, but a portion of the starting material was recovered from the reaction. By increasing the quantity of dimethylsulfate to 4 moles while maintaining the pH below 8, a reaction mass was obtained which contained no starting material. In this case two substances could be isolated from it: a dimethyl derivative (IV) and a trimethylderivative (Va or Vb). Isolation of the trimethyl derivative and its characterization entailed practically no difficulty, since it is very excellently soluble in water and considerably less soluble in organic solvents (including chloroform). In order to isolate it from the dimethyl derivative, it was necessary to render the solution obtained after methylation alkaline, and repeatedly to extract it with a large quantity of chloroform. The trimethylderivative crystallized in the form of a crystalline monohydrate with a m.p. of 105-107°. Upon drying it lost 1 mole of water of crystallization and melted at 192-193°. The dimethyl derivative was at once extracted from the acidified solution after completion of the extraction of the trimethylderivative with chloroform. The total yield of substances (IV) and (V) exceeded 80% of the theoretical.

Methylation of 4 moles of dimethylsulfate at a higher pH (8-10) leads to the formation of a mixture of (V) with another substance (VIa). Compound (VIa) crystallized in the form of prisms and melted at 223-224°. According to analysis it consisted of a tetramethyl derivative of the intermediate substance in which all four methyl groups are linked to the nitrogen atoms of the ring; the presence of the methoxy group in it was not detected even in traces. The tetramethyl derivative (VI) can also be obtained from compounds (IV) and (V). By careful methylation of the dimethyl derivative with a stoichiometric quantity of dimethyl sulfate, the formation of the trimethyl derivative proceeds.

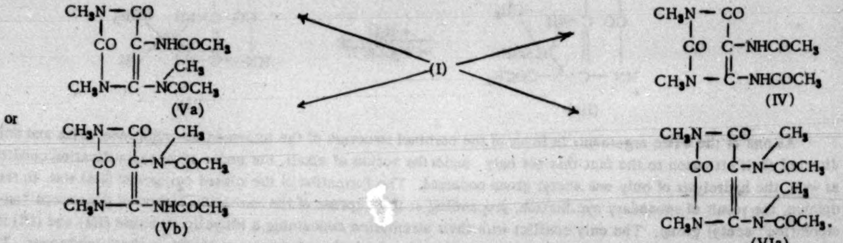
The preparation of a tetramethyl derivative in which all four methyl groups are linked with nitrogen atoms served as the first conclusive refutation of the views of Biltz and Schmidt on the structure of the intermediate substance: if it actually consisted of a bicyclic carbinol, acetylated at one of its nitrogen atoms (IIa), then the replacement of all of its mobile hydrogens with methyl groups should lead to the preparation of compound (VII) containing a methoxy group:



(VII)

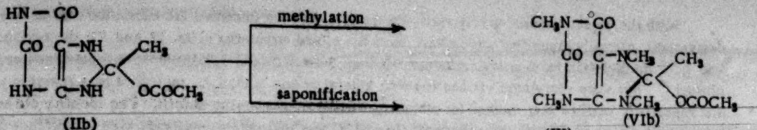
The absence of a methoxy group in the tetramethyl derivative seems an argument in favor of the assumption that it consists of 1,3-dimethyl-4,5-di-(acetylmethylamino)-uracil, while the initial, unmethylated intermediate substance would consist of 4,5-di-(acetylamino)-uracil (I) (in agreement with the initial representation of its structure that was rejected after the work of Biltz and Schmidt). In this case the di- and trimethyl derivatives should have the following structures set forth below (Scheme A):

Scheme A



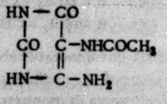
(Va) or (Vb) (I) (IV) (VIa)

The results obtained on the methylation of the intermediate substance thus demonstrate the incorrectness of the representation of the carbinol structure (IIa). It did not, however, provide a basis for excluding the probability of another cyclic structure in no way previously considered: it could be assumed that it consisted of a carbinol ester in which all four nuclear nitrogen atoms are linked with hydrogen atoms (or with methyl groups), while the acetyl group replaces hydrogen atoms not at the nitrogen, but at the hydroxyl group in position 8, with formation of an ester, but not of an amide bond (IIb). The possibility of such a structure is in complete agreement with the ability of only one acetyl group to undergo hydrolysis and with the absence of the reactions characteristic of the hydroxyl group. In this case the saponified intermediate substance would consist of a carbinol (III) of precisely that structure which was ascribed to it by Biltz and Schmidt, but the tetramethyl derivative would not contain the methoxy group (VIb):

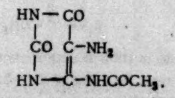


(IIb) (III) (VIb)

If the intermediate substance were 4,5-di-(acetylamino)-uracil (I) (Scheme A), then the substance obtained from it as a result of the saponification of one acetyl group should be one of the two following monoacetyl derivatives (VIII) of 4,5-diaminouracil:



(VIIIa)



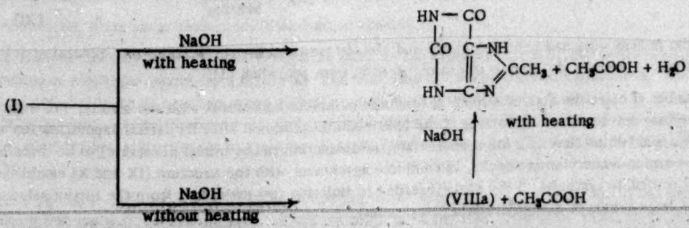
(VIIIb)

The establishment of the true structure of the saponified compound should thus resolve the question of the structure of the initial intermediate substance. The saponified substance was obtained according to the prescription of Biltz and Schmidt, i.e., in a reaction with 10% alkali in the cold. Its monomethyl derivative (IX), described by these same authors and the dimethyl derivative (X) were also obtained. All three compounds failed to react with acetic anhydride in the cold or with acetic acid on heating.

The absence of reaction with acetic acid at once completely excludes the probability of structure (VIIIb), since amino groups bound to a pyrimidine ring in position 5 are always readily alkylated on heating with carboxylic acids [5].

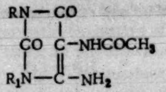
A choice remains between the two possible structures – the closed (III) and the open (VIIIa). In the case of structure (VIIIa) the acetylamino group in position 5, which is not saponified with alkali, should be readily saponified by mineral acid, as this is characteristic of 5-acylamino pyrimidines [6]. This turned out to be the case, as was shown by the results of quantitative determinations of the acetyl group in the substance under investigation and in its two methylated derivatives (IX) and (X). The acetyl groups were subjected to hydrolysis by means of heating with 20% sulfuric acid. One mole of acetic acid was back-titrated in the distillate in all experiments. Saponification of both acetyl groups in the intermediate substance as the result of a sequential two-stage (first alkaline and then acidic) hydrolysis disposed of the basic argument of Biltz in favor of a cyclic carbinol structure for this compound.

On heating the substance under investigation (III or VIIIa) with alkali it is converted into 8-methylxanthine, i.e., conducts itself in a way characteristic of 5-amino-5-acylaminopyrimidines, which in such cases are cyclized with formation of purines. Such a reaction proceeds particularly readily with its mono- and dimethyl derivatives (IX) and (X) which are converted into the 3,8- and 1,3,8-methylxanthines. The intermediate substance can be at once converted into 8-methylxanthine by heating with 10% alkali, i.e., without preliminary saponification in the cold. This reaction with alkali can be expressed by the following scheme (if we start from the fact that it has the open structure (I):



The formation of 8-methylxanthine in this reaction completely explains the failures which have been encountered in the attempts to saponify both acetyl groups in the intermediate substance with alkali and is found in complete agreement with the long established inequality of the amino groups in 4,5-diaminopyrimidines. Only one acetylamino group is saponified in the cold (in position 4), while the other, more stable, remains untouched. Upon heating, cyclization at the expense of the carbonyl carbon of the second amino group (in position 5) occurs. If the reaction is conducted at once during heating, both processes apparently proceed simultaneously.

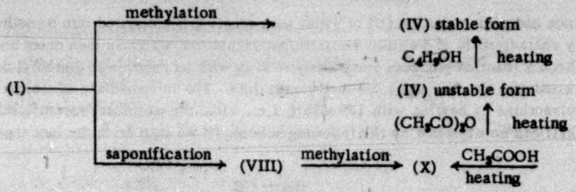
With the object of conclusively verifying the fact that the intermediate substance and its two methylated derivatives, partially saponified with alkali, have the closed structures,(VIIIa, IX and X), the synthesis of 3-methyl- and 1,3-dimethyl-4-amino-5-acetylamino-uracils from 3-methyl- and 1,3-dimethyl-4,5-diaminouracils was accomplished.* They were acetylated via heating with glacial acetic acid, i.e., subjected to a reaction widely adopted and repeatedly verified as a method for preparing 4-amino-5-acylamino-uracils. The identity of the compounds obtained in these reactions with the substances (IX and X) was indisputably demonstrated by the fact that the latter, and consequently, the initial nonmethylated substance (VIII) consisted of 4-amino-5-acetylaminouracil:

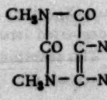


(VIII): R and R_1 = H;
(IX): R = H; $R_1 = CH_3$;
(X): R and $R_1 = CH_3$.

The establishment of their structure once more confirmed that the initial intermediate substance consisted of 4,5-di-(acetylamino)-uracil (I). One of its methylated derivatives (IV) was successfully synthesized from 1,3-dimethyl-4,5-diaminouracil (XI) in a reaction with acetic anhydride. The experiments demonstrated that such a reaction in the cold leads to the formation of a compound monoacetylated in position 5, while after boiling with acetic anhydride in the absence of base for 2 hours, a substance is separated which differs in its properties both from the initial 5-acetylderivative (X) and from the final 8-methyltheophylline formed as a result of the more prolonged reaction. It precipitates from the hot transparent solution in the form of coarse heavy crystals, slightly soluble in organic solvents and entirely unlike the expected substance (IV), which consists of soft, voluminous, cotton-like needles, quite soluble in chloroform in the cold and in the majority of organic solvents on heating. It does not differ from (IV) in melting point (207-209°, since a mixed sample of these two substances displays no melting point depression) or in its capacity to solidify after melting and secondarily melt at 315-325°. It does not differ in its total chemical composition.

Further conversions of the substance obtained showed that it apparently consisted of a dimorphous modification of compound (IV); it was successfully converted to the other form by heating for 2 hours with a large quantity of butyl alcohol (1: 75). During this the substance gradually went into solution and did not crystallize out on cooling. Only after keeping the solution in the cold for many hours did long, fine, soft-as-hair, crystals separate,—all the properties of substance (IV). Evidently, the modification obtained in the reaction with acetic anhydride is unstable on heating with butyl alcohol and is converted under these conditions into the stable form, identical with that obtained earlier as a result of methylation (I).





(XI)

When the present work had been completed and already prepared for publication, two general articles by Bredereck and his co-workers, devoted to this same question, were published [8].

In a number of cases the authors arrived at results in complete agreement with our results. For example, they consider the mono- and dimethyl derivatives of the intermediate substance after its partial saponification with alkali which they obtained (which they call the monoacetate, in distinction to the initial diacetate) to be 1-methyl- and 1,3-dimethyl-4-amino-5-acetylaminouracils, in complete agreement with the structure (IX and X) established by us and proved by reversible synthesis. They also succeeded in isolating two substances from the methylation of the diacetate with a large excess of dimethylsulfate (6-14 moles).

Judging by the described properties and by analysis, these substances (the dimethyl- and tetramethyldiacetates) are doubtless identical with the di- and tetramethyl derivatives (IV) and (VI). The authors state that they did not succeed in obtaining other methylated derivatives of the diacetate. In particular, they did not succeed in preparing the trimethyl derivative (V) described by us apparently, because of the difficulty of isolating and characterizing this very highly water-soluble compound.

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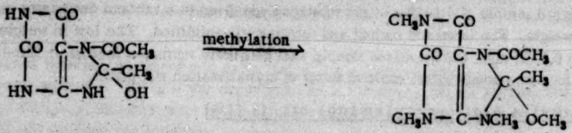
* 3-Methyl-4,5-diaminouracil was obtained by the reduction of 3-methyl-4-amino-5-isonitrosouracil (an intermediate product in the synthesis of theobromine); 1,3-dimethyl-4,5-diaminouracil was synthesized according to the directions of the Polish chemists Bobranski and Synowiedski [7].

It is impossible to agree with the conclusions of these authors with reference to the structure of the intermediate substance (diacetate),* which they consider to be a cyclic carbinol, differing with Biltz only on the question of the location of the acetyl group (at the nitrogen in position 7 and not 9).

Thus, they ascribe the following structure, identical with compound (VI) obtained by us, to the diacetate and its tetramethyl derivative:



At the same time they completely ignore the fact of the absence in the latter of the methoxy group, which completely disproves the probability of the structure set forth by them.

Ignoring the absence of the methoxy group in the tetramethyldiacetate, the authors base the cyclic structure for the diacetate and its methylated derivatives chiefly on the comparison of the properties of the two dimethyldiacetates obtained by them. They consider one dimethyldiacetate to be of an open structure, i.e., 1,3-dimethyl-4,5-di-(acetylamino)-uracil; the other – identical with the compound (IV) described by us – to be the closed form. The authors indicate that the diacetate with an open structure is converted into the closed form by the action of alkali, but do not direct their attention to the contradiction which is involved in their assumption that in the case of the conversion of the open diacetate into the closed form the action of alkali evokes cyclization, while in the case of conversion of the diacetate into the monoacetate it evokes opening of the ring. On the basis of our work it seems much more probable that the dimethyldiacetates obtained by the foreign authors, are not structurally different, but are the two modifications described above of 1,3-methyl-4,5-di-(acetylamino)-uracil (IV), of which one form (obtained in the reaction with acetic anhydride) can be converted into the other by heating with alcohol.

EXPERIMENTAL

1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (V)

8 ml of 32.5% NaOH solution and 8 ml of dimethylsulfate were simultaneously added at an equal rate to a suspension of 5 g of the intermediate substance (I) in 30 ml of water at a temperature of 30-35°. The duration of the addition was 4 hours. The reaction medium was kept alkaline to litmus but neutral to phenolphthalein (pH below 8). The transparent solution was treated with carbon, filtered, rendered alkaline to a pH of 9 and repeatedly extracted with chloroform (the extraction progresses very slowly). The residue after distilling off the chloroform – 4.2 g of slowly congealing oil – was treated with 10 ml of dry acetone. On rubbing with a rod a portion of the substance dissolves, and a portion crystallizes. Dry sulfuric ether (30-40 ml) was poured in and the crystalline mass was drawn off. The weight was 3.64 g, the m.p. 172-174°. It was boiled 3 times with dry benzene and the crystals were drawn off from the hot suspension.

The melting point under these conditions rose to 186-189.5°.

For analysis the substance was dissolved in dry dioxane and ether was added to the solution; m.p. 192-193°. Coarse prisms or elongated plates were obtained. The substance was very excellently soluble in water, soluble in acetone, almost insoluble in benzene, even on boiling, and slightly soluble in sulfuric ether. It was moderately soluble in chloroform, crystallized from alcohol, methylethyl ketone, ethyl acetate and other solvents. When crystallized from solvents containing traces of moisture, it crystallized out with 1 mole of water of crystallization (m. p. 105-107°).

3.600 mg sub.: 5.31 ml 0.01 N H_2SO_4. 3.632 mg sub.: 5.39 ml 0.01 N H_2SO_4. 4.171 mg sub.: 7.511 mg CO_2; 2.178 mg H_2O. 4.712 mg sub.: 8.443 mg CO_2; 2.493 mg H_2O. Found %: N 20.65, 20.74; C 49.14, 48.90; H 5.84, 5.92. $C_{11}H_{16}O_4N_4$. Calculated %: N 20.89; C 49.2; H 6.00.

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* The authors consider the true intermediate substance in the reaction of the formation of 8-methylxanthine from uric acid to be not the diacetate but the triacetate. The hydrolysis of the third acetyl group and the formation of the diacetate proceeds, in their opinion, as early as the process of crystallization of the triacetate from water. Since boiling with water apparently should not evoke profound structural changes, this question is not touched upon here; it is not relevant to the elucidation of what structure – closed or cyclic – the intermediate substance has.

Preparation of the Monohydrate. 0.95 g of anhydrous substance with a m.p. of 192-193° was crystallized from 10 ml of distilled but not dried methylethyl ketone. 0.6 g of coarse transparent prisms with a m.p. of 105-107° precipitated. An additional 0.25 g with the same melting point precipitated from the filtrate during the addition of ether. It was dried for 24 hours in a vacuum desiccator over H_2SO_4 for analysis.

4.471 mg sub.: 6.27 ml 0.01 N H_2SO_4. 6.167 mg sub.: 8.72 ml 0.01 N H_2SO_4. Found %: N 19.65, 19.79. $C_{11}H_{16}O_4N_4 \cdot H_2O$. Calculated %: N 19.58.

A weighed sample of 0.1018 g of the substance was dried in a vacuum desiccator at 100° over calcium chloride to constant weight. The substance melted and subsequently solidified. The loss in weight was 0.0063 g, which amounted to 6.19%; m.p. 188°; a mixed sample with anhydrous substance melted at 188-192°. The calculated amount of moisture for a compound with 1 mole of water of crystallization was 6.29%.

1,3-Dimethyl-4,5-di-(acetylamino)-uracil (IV)

a) Preparation from 4,5-di-(acetylamino)-uracil (I). The water-alkali solution from the experiment described above which had been extracted with chloroform was acidified to a weakly acidic reaction as indicated by Congo red and extracted a second time with chloroform. The residue after distilling off the chloroform (1.1 g) crystallized from alcohol. Very fine fluffy needles with a m.p. of 206-207.5° were obtained. The melting point of a mixed sample with methylcaffeine was sharply depressed.

The substance was slightly soluble in cold water and quite soluble in hot water, from which it crystallized on cooling. It dissolved in alkaline solutions and precipitated on acidification; it was almost insoluble in benzene, even on boiling, was slightly soluble in hot acetone and in carbon tetrachloride, somwhat more so in ethyl acetate, and was satisfactorily soluble in chloroform. It crystallized in very fine thread-like needles from all the solvents. It crystallized from alcohol 1:30. It melted at 208-209°. On further heating, it evolved bubbles, subsequently solidified at 225° and again melted at 315-320°.

4.918 mg sub.: 7.65 ml 0.01 N H_2SO_4. 3.118 mg sub.: 4.83 ml 0.01 N H_2SO_4. 2.970 mg sub.: 5.159 mg.: CO_2; 1.607 mg H_2O. 3.723 mg sub.: 6.478 mg CO_2; 1.959 mg H_2O. Found %: N 21.78, 21.70; C 47.38, 47.45; H 6.04, 5.88. $C_{10}H_{14}O_4N_4$ Calculated %: N 22.04; C 47.20; H 5.51.

b) Preparation from 1,3-dimethyl-4-amino-5-acetylaminouracil (X). A mixture of 3 g of 1,3-dimethyl-4-amino-5-acetylaminouracil with 30 ml of freshly distilled acetic anhydride was placed in an oil bath heated to 130°. It was boiled two hours after which the hot transparent solution was poured off from the coarsely crystalline substance into another flask. On cooling this solution, 0.45 g of material crystallized out from it in the form of needles with a m.p. of 315° which was shown to be identical with 8-methyltheophylline. The acetic anhydride was distilled off in a vacuum. The residue – 0.87 g with a m.p. of 180-196° – crystallized from a large quantity of alcohol. Small, heavy, transparent prisms with a m.p. of 207-209° precipitated.

The coarsely crystalline, transparent substance (1.8 g) isolated directly from the reaction melted at the same temperature. It was almost insoluble, even on boiling, in ethyl acetate, benzene, chlorobenzene, methylethyl ketone, very slightly soluble in chloroform and alcohol, somewhat more soluble in water. It reduced an ammoniacal solution of silver oxide.

A mixed specimen with (IV) obtained by method "a" melted at 207-209°.

It was crystallized from 100 ml of butyl alcohol. It all went into solution as a result of prolonged boiling, but on cooling did not precipitate for a long time. After prolonged standing in a condenser, a voluminous precipitate of very soft long needles impregnated with coarse prisms, separated from the transparent solution obtained; these needles were readily soluble in chloroform and other organic solvents and melted at 207°. The mixture of crystals was heated to the boiling point with 30 ml of alcohol, whereupon the needles at once dissolved, while the insignificant precipitate of coarse heavy crystals was left in the flask for a day. Their weight was 0.14 g; their melting point 207-208°. The crystals were cloudy under the microscope; evidently they were in the process of conversion to the needles.

All three substances obtained in reaction "a" and also the prisms from reaction "b" and their mixtures melted at an identical temperature. However, on further heating the melted substance evolved bubbles of gas (224-225°) and solidified. In all cases the solidified substance began to melt at 315-320°. For analysis the substance was crystallized from alcohol and dried in a vacuum desiccator over H_2SO_4.

3.060 mg sub.: 4.78 ml 0.01 N H_2SO_4. 3.689 mg sub.: 5.79 ml 0.01 N H_2SO_4. 3.606 mg sub.: 6.258 mg CO_2; 1.830 mg H_2O. 4.189 mg sub.: 7.240 mg CO_2; 2.183 mg H_2O. Found %: N 21.87, 21.96; C 47.36, 47.17; H 5.68, 5.83. $C_{10}H_{14}O_4N_4$. Calculated %: N 22.04; C 47.20; H 5.51.

1,3-Dimethyl-4,5-di-(acetylmethylamino)-uracil (VIa)

a) Preparation from 4,5-Di-(acetylamino)-uracil (I). 8.5 ml of a 32.5% solution of NaOH and 9 ml of dimethylsulfate were added to a suspension of 5 g of (I) in 30 ml of water at a temperature of 30-35°. It was preliminarily drenched with 3 ml of alkali after which the addition of both reagents was conducted simultaneously at a pH of 9-10. After completion of the reaction the solution treated with carbon and filtered, was alkaline to phenolphthalein and was exhaustively extracted with chloroform. The residue after distilling off the chloroform (4.6 g) was crystallized from 35 ml of alcohol. Elongated flakes crystallized out with a m.p. of 222-224°. The weight was 1.85 g. Ether was added to the alcoholic filtrate. 2.3 g of the monohydrate (V) with m.p. 105-107° was isolated by this means.

Nothing was extracted by repeated chloroform extraction of the aqueous solutions (after acidification). Material with m.p. 222-224° was crystallized from alcohol (1: 16) for analysis. Fine and transparent rectangular plates with m.p. 223-224° were obtained. The material was quite soluble in cold water and the addition of alkali did not increase the solubility. It was slightly soluble in acetone and ethyl acetate in the cold, more soluble on heating, and crystallized in the form of plates. It dissolved in boiling alcohol (6: 100) and was almost insoluble in benzene, even on heating.

1.664 mg substance: 2.40 ml 0.01N H_2SO_4. 1.815 mg substance: 2.63 ml 0.01 N H_2SO_4. 3.830 mg substance: 7.186 mg CO_2; 2.158 mg H_2O. 3.509 mg substance: 6.553 mg CO_2; 1.957 mg H_2O. Found %: N 20.19, 20.28; C 51.17, 50.93; H 6.13, 6.24; OCH_3 and OH (not detected). $C_{12}H_{18}O_4N_4$. Calculated %: N 19.82; C 51.06; H 6.36.

b) Preparation from 1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (Va). 0.25 ml of 32.5% solution of NaOH and 0.25 ml of dimethylsulfate were added alternately, in drops, to a solution of 0.5 g of substance (Va) with m.p. 186-189° in 5 ml of water. The reaction was conducted at pH 9-10 and a temperature of 30-35° for 1.5 hours. The solution which was alkaline to thymolphthalein was extracted with chloroform (the extraction was quickly completed) and the chloroform was distilled off. The crystalline residue with m.p. 205° was crystallized from alcohol. Characteristic transparent plates with m.p. 223-223.5° were obtained. A mixed specimen with the substance obtained as a result of the methylation of 4,5-di-(acetylamino)-uracil at a pH of 8-10 displayed no melting point depression; a mixed specimen with the starting material began to melt at 172°.

c) Preparation from 1,3-Dimethyl-4,5-di-(acetylamino)-uracil (IV). 0.45 ml of a 33% NaOH solution and 0.5 ml of dimethylsulfate were poured simultaneously and dropwise, into a suspension of 0.5 g of substance (IV) in 3 ml of water while the suspension was being stirred. The pH of the solution was about 9 during the reaction. The alkaline solution was extracted with chloroform. The residue after distilling off the chloroform was crystallized from alcohol. The weight was 0.45 g and the m.p. 223-224°. The melting point of a mixed specimen with the preceding was not depressed. Nothing was extracted by chloroform from the extracted solution after its acidification.

1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (V)

Preparation from 1,3-dimethyl-4,5-di-(acetylamino)-uracil (IV). 0.2 ml of a 32.5% alkali solution and 0.2 ml of dimethylsulfate were added alternately, in drops, and during intensive stirring, to a suspension of 0.5 g of substance (IV) (m.p. 206-207°) in 5 ml of water. The duration of the reaction (at pH 8) was 1.5 hours. The alkaline solution was repeatedly extracted with chloroform and the residue after distilling off the chloroform was treated with dry acetone and ether. The substance which crystallized was separated and boiled twice with dry benzene; m.p. 179°. The melting points of mixed samples were as follows: 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil with (Va), obtained as a result of the methylation of 4,5-di-(acetylamino)-uracil (I) (m.p. 186-189°) 179-184°; with (VIa) obtained by the same method (m.p. 223-224°) 164-167°; with the starting material (IV) melting began at 166° and melting occurred at 172-174°.

The characteristic transparent prisms of the monohydrate with m.p. 105-107° were obtained after crystallization from moist methylethyl ketone.

The chloroform-extracted solution was acidified and again extracted with chloroform. The residue after distilling off the chloroform was crystallized from alcohol; m.p. 207°. A mixed specimen with the initial material melted at 206-207°.

4-Amino-5-acetylaminouracil (VIII)

30 g of 4,5-di-(acetylamino)-uracil (I) was dissolved in 300 ml of 10% NaOH solution. The solution was shaken with carbon, filtered and left to stand at room temperature for 10 days. It was acidified with 10% H_2SO_4

to a weakly acidic reaction as indicated by Congo red, cooled to complete precipitation of the material, and filtered. Bright yellow elongated plates were obtained. The weight was 16.1 g. The material was crystallized from 900 ml of water. The mother liquor was concentrated in a vacuum and the substance thereby isolated was crystallized again from water. The total yield of recrystallized substance was 12 g.

4.320 mg substance: 6.221 mg CO_2; 1.663 mg H_2O. 3.460 mg substance: 4.984 mg CO_2; 1.270 mg H_2O. Found %: C 39.29, 39.31; H 4.34, 4.10. $C_6H_8O_3N_4$. Calculated %: C 39.13; H 4.34

3-Methyl-4-amino-5-acetylaminouracil (IX)

a) Preparation from 4-Amino-5-acetylaminouracil (VIII). 8 ml of dimethylsulfate was added to a filtered solution of 3.7 g of 4-amino-5-acetylaminouracil in 26 ml of 5.6% KOH solution and the reaction mass was periodically shaken for 1 hour. The formation of fine white needles began after 20 minutes. It was left to stand for 3 hours, after which it was filtered and the residue washed with alcohol and ether. The weight was 2.8 g, the m.p. 276-278°. On standing, 0.24 g more of the same needles separated from the filtrate. The total yield consequently amounted to 1.5 g (65%).

The material was crystallized from 100 ml of aqueous alcohol (1: 1). The twice-crystallized substance melted at 285°. It was dried for 24 hours in a vacuum desiccator for analysis. Fine white needles, soluble in water and insoluble in chloroform, were obtained. The substance dissolved in alkalis and separated from the alkaline solution on acidification. It crystallized from a large quantity of alcohol.

2.190 mg substance: 3.76 ml 0.01 N H_2SO_4. 3.920 mg substance: 6.69 ml 0.01 N H_2SO_4. 3.792 mg substance: 4.945 mg CO_2; 2.027 mg H_2O. 5.229 mg substance: 6.800 mg CO_2; 2.811 mg H_2O. 0.2568 g substance: 0.0376 g H_2O — loss on drying (150°). Found %: N 24.03, 23.90; C 35.58, 35.49; H 5.98, 6.01; H_2O 14.5. $C_7H_{10}O_3N_4 \cdot 2H_2O$. Calculated %: N 23.93; C 35.90; H 6.00; H_2O 15.3.

b) Preparation from 3-Methyl-4,5-diaminouracil. 2 g of 3-methyl-4,5-diaminouracil and 20 ml of glacial acetic acid were boiled for 4 hours with a reflux condenser. After cooling, the crystallized mass was filtered and washed with ether. The weight was 2.42 g, the m.p. 292-293°. A mixed specimen with the material obtained by method "a" had m.p. 292°. It was crystallized from 100 ml of aqueous alcohol (1: 1). 0.4935 g of the substance lost 0.0756 g on drying at 140°, i.e., weight loss on drying 15.3%. An ammoniacal solution of silver oxide was reduced with formation of a mirror.

1,3-Dimethyl-4-amino-5-acetylaminouracil (X)

a) Preparation from 4-amino-5-acetylaminouracil (VIII). 4.1 ml of dimethylsulfate and 3.9 ml of 32.5% NaOH solution were added alternately, in 0.5 ml portions, during stirring, to a suspension of 3 g of 4-amino-5-acetylaminouracil in 10 ml of water. There was an interval between the addition of each portion of alkali of 5 minutes and of 20-25 minutes between the addition of each portion of dimethylsulfate. Everything gradually went into solution and then crystallized in a viscous mass. The reaction mixture was neutralized to a weakly acidic reaction as indicated by Congo red, filtered and the residue washed with ice water. The weight was 1.6 g and the m.p. 268-270° (traces of liquefaction at 262°). A mixed specimen with 3-methyl-4-acetylamino-5-aminouracil (m.p. 285°) melted at 255-262°, i.e., displayed a definite melting point depression. It was twice crystallized from alcohol for the analysis. Fine soft needles or elongated rectangular plates were obtained. An ammoniacal solution of silver oxide was reduced with the formation of a mirror. The material was quite soluble in water, soluble in hot alcohol 1: 60, almost insoluble in xylol, ethyl acetate, chloroform, even on heating. It crystallized in the form of needles from ethyl and butyl alcohols and a large quantity of methylethyl ketone: m.p. 280°.

3.201 mg substance: 5.94 ml 0.01 N H_2SO_4. 3.626 mg substance: 6.75 ml 0.01 N H_2SO_4. 3.085 mg substance: 5.179 mg CO_2; 1.491 mg H_2O. 4.082 mg substance: 6 762 mg CO_2; 2.041 mg H_2O. Found %: N 25.98, 26.07; C 45.54, 45.21; H 5.41, 5.60. $C_8H_{12}O_3N_4$. Calculated %: N 26.41; C 45.28; H 5.66.

b) Preparation from 3-Methyl-4-amino-5-acetylaminouracil (IX). 0.55 ml of dimethylsulfate was added to a solution of 1 g of 3-methyl-4-amino-5-acetylaminouracil in 2.8 ml of 8% NaOH solution. The mixture was shaken for 45 minutes whereupon the mass crystallized. It was filtered and the crystalline substance was washed with alcohol. The weight was 0.8 g and after a single crystallization from alcohol the m.p. was 264-268°. A mixed specimen with the starting material displayed a distinct melting point depression, with the dimethyl derivative obtained by method "a" melted at 264-268° and did not differ from it in other physical properties.

c) Preparation from 1,3-dimethyl-4,5-diaminouracil. 1) 5 g of 1,3-dimethyl-4,5-diaminouracil was boiled for 5 hours with 50 ml of glacial acetic acid. The acetic acid was distilled off from the transparent solution in a vacuum. The residue was treated with ether and separated. The weight was 5.75 g and the m.p. 265-266°. It was crystallized from alcohol. Fluffy white needles were obtained. There was no melting point depression in mixtures with the substances obtained by methods "a" and "b" and it did not differ from them in its properties. An ammoniacal solution of silver oxide was reduced in the cold with the formation of a mirror. 0.3 g was again crystallized from 20 ml of alcohol for the analysis.

4.290 mg substance: 8.04 ml 0.01 N H_2SO_4. Found %: N 26.28. $C_8H_{12}O_3N_4$. Calculated %: N 26.41.

2) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of acetic anhydride; some evolution of heat was observed. The mixture was left to stand for two weeks at room temperature in a flask with a ground stopper. In the course of this period the mass became somewhat more mobile. It was filtered and the white crystals obtained were washed with ether. The weight was 1.02 g and the m.p. 266-270°. Mixed samples with the substances obtained in the preceding (Preparation "c", Experiment 1) and succeeding (Preparation "c", Experiment 3) experiments did not display any melting point depression.

3) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of dry pyridine and 5 ml of acetic anhydride. The mixture was left to stand for 2 weeks at room temperature; it crystallized in this period. It was filtered and the crystalline residue was washed with ether. The weight was 1.1 g (92.7%) and the m.p. 271-272°. No melting point depression was detected in mixed specimens with samples of the materials obtained in the preceding experiments.

SUMMARY

The structures of the intermediate substance formed in the transformation reaction of uric acid into 8-methylxanthine and also of the compound obtained from it as a result of the hydrolysis of one acetyl group were studied. A series of methylated derivatives of these two substances was synthesized and described. It was found that all the compounds studied are mono- and diacetylated derivatives of 4,5-diaminouracil and not binuclear carbinols (8-hydroxy-8-methyl-8,9-dihydroxanthines). Some reactions and transformations of these compounds were studied.

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* See Consultants Bureau Translation, page 145.

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SUMMARY

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(1) German Patent [illegible]

(2) German Patent [illegible]

(3) [illegible]

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(6) [illegible]

(7) [illegible]

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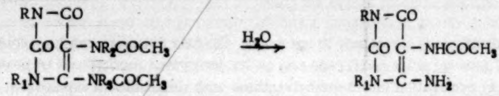
THE CONVERSION OF URIC ACID INTO 8-METHYLXANTHINE

II. ACTION OF MINERAL ACIDS ON 4,5-DI-(ACETYLAMINO)-URACIL

E. S. Golovchinskaya

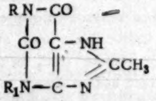
It was shown in the preceding communication [1] that the intermediate substance isolated in the conversion of uric acid into xanthine consists of 4,5-di-(acetylamino)-uracil (I). That paper included a description of the synthesis of three methylated derivatives of this substance (II, III and IV) and also of the mono- and dimethyl derivatives (VI and VII) of 4-amino-5-acetylaminouracil (V), obtained from (I) as a result of the hydrolysis of one acetyl group:



I: R, R_1, R_2 and $R_3 = H$
II: R and $R_1 = CH_3$; R_2 and $R_3 = H$
IIIa: R, R_1 and $R_3 = CH_3$; $R_2 = H$
IIIb: R, R_1 or $R_2 = CH_3$; $R_3 = H$
IV: R, R_1, R_2 and $R_3 = CH_3$

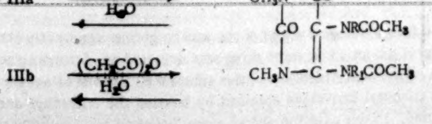
V: R and $R_1 = H$
VI: $R = H$; $R_1 = CH_3$
VII: R and $R_1 = CH_3$

On heating compound (I) and compound (V) obtained from it as a result of partial saponification with acetic anhydride, 8-methylxanthine (VIII)* is formed; (VI) is converted under these conditions into 3,8-dimethylxanthine (IX) characterized by methylation to 1,3,7,8-tetramethylxanthine while substances (II) and (VII) are converted into 8-methyltheophylline (X):



VIII: R and $R_1 = H$
IX: $R = H$; $R_1 = CH_3$
X: R and $R_1 = CH_3$

As was to be expected, heating the tetramethylderivative (IV) with acetic anhydride did not lead to cyclization. The starting material was quantitatively recovered from the reaction. The trimethyl derivative (III) was also not cyclized under these same conditions; it was acetylated with the formation of a substance which contained three acetyl groups (XI). A third acetyl group substituted for the unique labile hydrogen in molecule (III), is readily hydrolyzed with the formation of the initial compound, even when merely heated with water.



XIa: $R = COCH_3$; $R_1 = CH_3$
XIb: $R = CH_3$; $R_1 = COCH_3$

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* In this case and in all further work, 8-methylxanthine and its methylated derivatives were characterized by methylation to methylcaffeine.

to a weakly acidic reaction as indicated by Congo red, cooled to complete precipitation of the material, and filtered. Bright yellow elongated plates were obtained. The weight was 16.1 g. The material was crystallized from 900 ml of water. The mother liquor was concentrated in a vacuum and the substance thereby isolated was crystallized again from water. The total yield of recrystallized substance was 12 g.

4.320 mg substance: 6.221 mg CO_2; 1.663 mg H_2O. 3.460 mg substance: 4.984 mg CO_2; 1.270 mg H_2O. Found %: C 39.29, 39.31; H 4.34, 4.10. $C_6H_8O_3N_4$. Calculated %: C 39.13; H 4.34

3-Methyl-4-amino-5-acetylaminouracil (IX)

a) Preparation from 4-Amino-5-acetylaminouracil (VIII). 8 ml of dimethylsulfate was added to a filtered solution of 3.7 g of 4-amino-5-acetylaminouracil in 26 ml of 5.6% KOH solution and the reaction mass was periodically shaken for 1 hour. The formation of fine white needles began after 20 minutes. It was left to stand for 3 hours, after which it was filtered and the residue washed with alcohol and ether. The weight was 2.8 g, the m.p. 276-278°. On standing, 0.24 g more of the same needles separated from the filtrate. The total yield consequently amounted to 1.5 g (65%).

The material was crystallized from 100 ml of aqueous alcohol (1: 1). The twice-crystallized substance melted at 285°. It was dried for 24 hours in a vacuum desiccator for analysis. Fine white needles, soluble in water and insoluble in chloroform, were obtained. The substance dissolved in alkalis and separated from the alkaline solution on acidification. It crystallized from a large quantity of alcohol.

2.190 mg substance: 3.76 ml 0.01 N H_2SO_4. 3.920 mg substance: 6.69 ml 0.01 N H_2SO_4. 3.792 mg substance: 4.945 mg CO_2; 2.027 mg H_2O. 5.229 mg substance: 6.800 mg CO_2; 2.811 mg H_2O. 0.2568 g substance: 0.0376 g H_2O – loss on drying (150°). Found %: N 24.03, 23.90; C 35.58, 35.49; H 5.98, 6.01; H_2O 14.5. $C_7H_{10}O_3N_4 \cdot 2H_2O$. Calculated %: N 23.93; C 35.90; H 6.00; H_2O 15.3.

b) Preparation from 3-Methyl-4,5-diaminouracil. 2 g of 3-methyl-4,5-diaminouracil and 20 ml of glacial acetic acid were boiled for 4 hours with a reflux condenser. After cooling, the crystallized mass was filtered and washed with ether. The weight was 2.42 g, the m.p. 292-293°. A mixed specimen with the material obtained by method "a" had m.p. 292°. It was crystallized from 100 ml of aqueous alcohol (1: 1). 0.4935 g of the substance lost 0.0756 g on drying at 140°, i.e., weight loss on drying 15.3%. An ammoniacal solution of silver oxide was reduced with formation of a mirror.

1,3-Dimethyl-4-amino-5-acetylaminouracil (X)

a) Preparation from 4-amino-5-acetylaminouracil (VIII). 4.1 ml of dimethylsulfate and 3.9 ml of 32.5% NaOH solution were added alternately, in 0.5 ml portions, during stirring, to a suspension of 3 g of 4-amino-5-acetylaminouracil in 10 ml of water. There was an interval between the addition of each portion of alkali of 5 minutes and of 20-25 minutes between the addition of each portion of dimethylsulfate. Everything gradually went into solution and then crystallized in a viscous mass. The reaction mixture was neutralized to a weakly acidic reaction as indicated by Congo red, filtered and the residue washed with ice water. The weight was 1.6 g and the m.p. 268-270° (traces of liquefaction at 262°). A mixed specimen with 3-methyl-4-acetylamino-5-aminouracil (m.p. 285°) melted at 255-262°, i.e., displayed a definite melting point depression. It was twice crystallized from alcohol for the analysis. Fine soft needles or elongated rectangular plates were obtained. An ammoniacal solution of silver oxide was reduced with the formation of a mirror. The material was quite soluble in water, soluble in hot alcohol 1: 60, almost insoluble in xylol, ethyl acetate, chloroform, even on heating. It crystallized in the form of needles from ethyl and butyl alcohols and a large quantity of methylethyl ketone: m.p. 280°.

3.201 mg substance: 5.94 ml 0.01 N H_2SO_4. 3.626 mg substance: 6.75 ml 0.01 N H_2SO_4. 3.085 mg substance: 5.179 mg CO_2; 1.491 mg H_2O. 4.082 mg substance: 6 762 mg CO_2; 2.041 mg H_2O. Found %: N 25.98, 26.07; C 45.54, 45.21; H 5.41, 5.60. $C_8H_{12}O_3N_4$. Calculated %: N 26.41; C 45.28; H 5.66.

b) Preparation from 3-Methyl-4-amino-5-acetylaminouracil (IX). 0.55 ml of dimethylsulfate was added to a solution of 1 g of 3-methyl-4-amino-5-acetylaminouracil in 2.8 ml of 8% NaOH solution. The mixture was shaken for 45 minutes whereupon the mass crystallized. It was filtered and the crystalline substance was washed with alcohol. The weight was 0.8 g and after a single crystallization from alcohol the m.p. was 264-268°. A mixed specimen with the starting material displayed a distinct melting point depression, with the dimethyl derivative obtained by method "a" melted at 264-268° and did not differ from it in other physical properties.

c) Preparation from 1,3-dimethyl-4,5-diaminouracil. 1) 5 g of 1,3-dimethyl-4,5-diaminouracil was boiled for 5 hours with 50 ml of glacial acetic acid. The acetic acid was distilled off from the transparent solution in a vacuum. The residue was treated with ether and separated. The weight was 5.75 g and the m.p. 265-266°. It was crystallized from alcohol. Fluffy white needles were obtained. There was no melting point depression in mixtures with the substances obtained by methods "a" and "b" and it did not differ from them in its properties. An ammoniacal solution of silver oxide was reduced in the cold with the formation of a mirror. 0.3 g was again crystallized from 20 ml of alcohol for the analysis.

4.290 mg substance: 8.04 ml 0.01 N H_2SO_4. Found %: N 26.28. $C_8H_{12}O_3N_4$. Calculated %: N 26.41.

2) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of acetic anhydride; some evolution of heat was observed. The mixture was left to stand for two weeks at room temperature in a flask with a ground stopper. In the course of this period the mass became somewhat more mobile. It was filtered and the white crystals obtained were washed with ether. The weight was 1.02 g and the m.p. 266-270°. Mixed samples with the substances obtained in the preceding (Preparation "c", Experiment 1) and succeeding (Preparation "c", Experiment 3) experiments did not display any melting point depression.

3) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of dry pyridine and 5 ml of acetic anhydride. The mixture was left to stand for 2 weeks at room temperature; it crystallized in this period. It was filtered and the crystalline residue was washed with ether. The weight was 1.1 g (92.7%) and the m.p. 271-272°. No melting point depression was detected in mixed specimens with samples of the materials obtained in the preceding experiments.

SUMMARY

The structures of the intermediate substance formed in the transformation reaction of uric acid into 8-methylxanthine and also of the compound obtained from it as a result of the hydrolysis of one acetyl group were studied. A series of methylated derivatives of these two substances was synthesized and described. It was found that all the compounds studied are mono- and diacetylated derivatives of 4,5-diaminouracil and not binuclear carbinols (8-hydroxy-8-methyl-8,9-dihydroxanthines). Some reactions and transformations of these compounds were studied.

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* See Consultants Bureau Translation, page 145.

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SUMMARY

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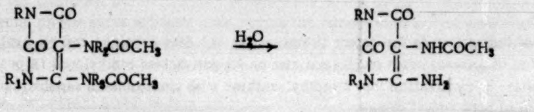
THE CONVERSION OF URIC ACID INTO 8-METHYLXANTHINE

II. ACTION OF MINERAL ACIDS ON 4,5-DI-(ACETYLAMINO)-URACIL

E. S. Golovchinskaya

It was shown in the preceding communication [1] that the intermediate substance isolated in the conversion of uric acid into xanthine consists of 4,5-di-(acetylamino)-uracil (I). That paper included a description of the synthesis of three methylated derivatives of this substance (II, III and IV) and also of the mono- and dimethyl derivatives (VI and VII) of 4-amino-5-acetylaminouracil (V), obtained from (I) as a result of the hydrolysis of one acetyl group:



I: R, R_1, R_2 and R_3 = H

II: R and R_1 = CH_3; R_2 and R_3 = H

IIIa: R, R_1 and R_3 = CH_3; R_2 = H

IIIb: R, R_1 or R_2 = CH_3; R_3 = H

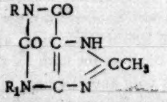
IV: R, R_1, R_2 and R_3 = CH_3

V: R and R_1 = H

VI: R = H; R_1 = CH_3

VII: R and R_1 = CH_3

On heating compound (I) and compound (V) obtained from it as a result of partial saponification with acetic anhydride, 8-methylxanthine (VIII)* is formed; (VI) is converted under these conditions into 3,8-dimethylxanthine (IX) characterized by methylation to 1,3,7,8-tetramethylxanthine while substances (II) and (VII) are converted into 8-methyltheophylline (X):

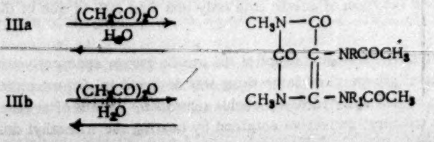


VIII: R and R_1 = H

IX: R = H; R_1 = CH_3

X: R and R_1 = CH_3

As was to be expected, heating the tetramethylderivative (IV) with acetic anhydride did not lead to cyclization. The starting material was quantitatively recovered from the reaction. The trimethyl derivative (III) was also not cyclized under these same conditions; it was acetylated with the formation of a substance which contained three acetyl groups (XI). A third acetyl group substituted for the unique labile hydrogen in molecule (III), is readily hydrolyzed with the formation of the initial compound, even when merely heated with water.



XIa: R = $COCH_3$; R_1 = CH_3

XIb: R = CH_3; R_1 = $COCH_3$

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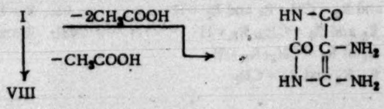
*In this case and in all further work, 8-methylxanthine and its methylated derivatives were characterized by methylation to methylcaffeine.

The experiments involving saponification of (I) and its methylated derivatives by various dilute acids – phosphoric and sulfuric – set up to account for the formation of acetic acid, at once refuted the assertion of Biltz and Schmidt [2] to the effect that the action of mineral acids as well as that of alkalis, leads to the hydrolysis of only one acetyl group. As a matter of fact, the quantity of acetic acid distilled off exceeded 1 mole in all cases. This amount varied from 1.12 to 1.41 moles under various acidic hydrolysis conditions, but did not once reach 2 moles.

Substance	Methods of saponification	Acetyl groups (in %)
(I)	Saponification with 1 N NaOH, acidified with sulfuric acid.	167.4
(I)	Saponification with 1 N NaOH, acidified with phosphoric acid	180.0
(I)	Saponification with phosphoric acid	112.5 Note. The elimination of acetic acid proceeded slowly and was not carried to completion.
(I)	Saponification with sulfuric acid	141.3
(II)	Saponification with sulfuric acid	126.0
(III)	Saponification with sulfuric acid	101.5
Acetylated derivative (III)	Saponification with sulfuric acid	200.9

On the basis of indications in the patent literature [3], the data obtained can be explained by the assumption that during the action of mineral acids on (I) (and also on its derivatives methylated in positions 1 and 3) two parallel processes proceed: a) cyclization into 8-methylxanthine with simultaneous saponification of one acetyl group and b) saponification of both acetyl groups.

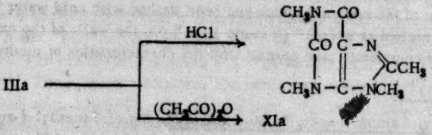


The 4,5-diaminouracil formed in this second process can be subjected to further irreversible conversions (hydrolysis of the amino group in position 4, oxidation and others).

Study of the substances formed as a result of boiling (I) with 10% hydrochloric acid, completely confirmed that, in this case, the saponification reaction is accompanied by cyclization. Comparatively pure, high grade methylxanthine was characterized by methylation to 8-methylcaffeine, was isolated from the reaction mixture. Its yield varied in various experiments, depending on the concentration of hydrochloric acid, approaching 50% of the theoretical in the best case, which was in complete agreement with the data set forth for the quantitative determination of the acetyl groups in compound (I). It appears probable that if both acetyl groups in compound (I) could not be saponified either in acid or in alkaline media by way of cyclization, accompanied in both cases by a saponification process, then the hydrolysis of 1,3-dimethyl-4,5-di-(acetylmethylamino)-uracil (IV) has to proceed otherwise. The possibility of cyclization with evolution of acetic acid molecules is excluded by the absence of free hydrogen atoms in it; it could therefore be expected that the hydrolysis of this compound would lead to the quantitative saponification of both acetyl groups and the formation of 1,3-dimethyl-4,5-di-(aminomethyl)-uracil. Actually, however, attempts to hydrolyze compound (IV) gave unexpected results. Its saponification and, consequently, the elimination of acetic acid proceeded very slowly: after 2 days of heating with acid and distilling off in the form of vapor it was possible to titrate in the distillate in the form of acetic acid only less than 60% of one of the acetyl groups (i.e., about 30% of the total quantity).

The presence of methyl groups bound to the nitrogen atoms of the amino groups apparently stabilizes the bond between these nitrogen atoms and acetyl groups. The same thing was detected in, for example, the trimethyl derivative (III) (see the table). As a result of the acid hydrolysis of this substance, 1 mole of acetic acid was collected in a receiving flask, while with the triacetyl derivative obtained by heating the trimethyl derivative (III) with acetic anhydride, 2 moles were obtained. In this case the acetyl group bound to the methylated amino group is evidently very stable and did not undergo hydrolysis.

The further study of the structure of the substance formed in the reaction of the trimethyl derivative (III) with mineral acid was undertaken with the object of determining the position of the third methyl group in the molecule (III) (structure "a" or "b"). A substance was isolated in excellent yield (77%), from the experiments of heating (III) with 10% hydrochloric acid, which melted at 254° and possessed the physical properties which were described for 8-methylisocaffeine. The analysis and chemical behavior of this substance confirmed that it actually was 1,3,8,9-tetramethylisoxanthine. Its formation was absolute proof of the fact that the trimethylderivative (III) has the structure "a", i.e., consists of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil. In addition, it demonstrated that ring closure by the action of mineral acids, in the absence of cyclization evoked by acetic anhydride, does not require the presence of unsubstituted hydrogen in the acetylated amino group in position 4.



The results obtained permit certain conclusions to be drawn concerning the origin of the carbon in position 8 and the methyl group bound to it in 8-methylxanthines obtained as a result of various cyclization methods. The acetyl group bound to the amino group in position 4 should apparently be considered responsible for the closure of the imidazole ring during the action of mineral acids. Evidence in favor of this includes: a) the formation of 8-methylisocaffeine from the trimethyl derivative (III) in which the acetyl group in position 4 is stabilized by the presence of a methyl group on the same nitrogen atom, while the evolution of acetic acid must consequently occur at the expense of hydrolysis of the acetylamino group in position 5; and b) the quantitative saponification of the acetyl group in position 5 in 4-amino-5-acetylaminouracils on heating with mineral acids [1].

On the other hand, the acetyl group in position 5 indisputably participates in alkaline cyclization. This follows from the conversion of 4-amino-5-acetylaminouracils into methylxanthine by the action of alkali [1] and from the widely used method of preparing purines from 4-amino-5-acylaminopyrimidines.

Insufficient experimental data are available to exclude entirely the possibility of parallel participation of the acetyl group in position 4 in the alkaline cyclization of 4,5-di-(acetylamino)-uracil (I), but the readiness with which this group is saponified by alkali, even in the cold [2], renders this improbable.

A third question: which of the two acetyl groups is responsible for the synthesis of the imidazole ring in the reaction of 4,5-diaminouracils with acetic anhydride, is the subject of further investigation on the part of the author.

EXPERIMENTAL

8-Methylxanthine (VIII)

a) Preparation from 4,5-Di-(acetylamino)-uracil (I) via Heating with Mineral Acids. 2 g of 4,5-di-(acetylamino)-uracil and 10 ml of 10% HCl were boiled on iron gauze with a reflux condenser for 30 minutes. The reaction mixture at once foamed up, the substance quickly went into solution and the solution rapidly became cherry-red and then (after 10-15 minutes) straw-yellow. After cooling, crystals precipitated which were separated and washed with alcohol. The weight was 1 g and the content of methylxanthine according to analysis was 75.3%. Ammoniacal solution of silver oxide was reduced with formation of a mirror.

0.25 g of the substance was dissolved in 4 ml of 6% NaOH solution and methylated with 0.57 ml of dimethylsulfate. The solution crystallized only by the introduction of a seed crystal of methylcaffeine. The crystals were separated and washed with ice water. The weight was 0.1 g and the m.p. 207-208°. A mixed specimen with methylcaffeine did not display any depression of the melting point.

0.5 g of the substance was boiled with 20 ml of water, drawn off while hot and this operation was again repeated. The weight of the residue was 0.3 g (41.1%) and the methylxanthine content according to analysis was 99.4%. An ammoniacal solution of silver oxide was not reduced. 0.3 g of the washed-off substance obtained was methylated in 3.2 ml of 6% NaOH by the addition of 0.5 ml of dimethylsulfate. The solution formed a uniform crystalline mass even in the process of adding the dimethylsulfate. The melting point of the methylcaffeine obtained was 209-210°. A mixed specimen with methylcaffeine melted at 207-208°.

b) Preparation via Heating with Alkali. 2.25 g of 4,5-di-(acetylamino)-uracil and 4 ml of 10% NaOH solution were heated while being stirred on a boiling water bath for 2 hours. The reaction mass, viscous at the beginning, became liquid and acquired a reddish coloration. The reaction mixture crystallized on cooling. The substance which separated was transferred to a solution by addition of water and 20% NaOH solution. The turbid reddish solution which was obtained was filtered and acidified with 18% HCl. The yellow precipitate which thereupon separated out was separated and washed with water. The weight was 1.22 g. The residue was boiled with 40 ml of water and drawn off while hot. The weight was 0.74 g (46%); the content of methylxanthine according to analysis was 94.4%.

The substance obtained did not reduce an ammoniacal solution of silver oxide and did not evolve bubbles on heating with dilute nitric acid.

0.4 g was dissolved in 4.5 ml of 8% NaOH solution and methylated at 25-30° with 0.9 ml of dimethyl sulfate. An abundant evolution of methylcaffeine crystals was observed even during the process of methylation. The weight was 0.3 g and the melting point of the substance which had been washed with cold water was 202-205°. A mixed specimen with methylcaffeine melted at 204-207° (it came loose from the walls of the capillary at 202°). It crystallized from water in the form of completely pure crystals with the characteristics of methylcaffeine.

3,8-Dimethylxanthine (IX)

Preparation from 3-Methyl-4-amino-5-acetylaminouracil (VI). 2 g of 3-methyl-4-amino-5-acetylaminouracil and 4 ml of 10% NaOH solution were stirred on a boiling water bath for 2 hours. After cooling, 10% NaOH solution was added until the substance was entirely dissolved and the solution obtained was filtered and acidified with 18% HCl. The weight of the substance which thereupon separated, crystallizing in the form of fine needles, was 1.7 g; it did not melt on heating to 310°, but reduced ammoniacal solution of silver oxide (evidently, the substance obtained contained some admixture of the starting open acetylamino derivative). It crystallized from water in the form of needles.

1 g of the substance was boiled twice with 50 ml of alcohol; 0.2 g of material with m.p. 290-291° did not dissolve (the starting material). 0.6 g of white needles precipitated from alcohol on cooling. An ammoniacal solution of silver oxide was reduced very slowly.

0.5 g of the substance obtained was dissolved in 4.5 ml of 8% NaOH solution. The solution was methylated with 1 ml of dimethylsulfate. The entire mass crystallized even during the addition of dimethylsulfate (with the pH of the solution above 9). The melting point of the washed substance obtained was 207-208°. A mixed specimen with methylcaffeine melted at the same temperature.

8-Methyltheophylline (X)

a) Preparation from 1,3-Dimethyl-4,5-di-(acetylamino)-uracil (II). 0.5 g of 1,3-dimethyl-4,5-di-(acetylamino)-uracil and 10 ml of freshly prepared acetic anhydride were boiled for 30 hours. The substance went into solution at 120°. The crystals which precipitated on cooling were separated and washed with alcohol and ether. They consisted of needles with m.p. 315-320° and a weight of 0.15 g. The acetic anhydride was distilled off from the filtrate in a vacuum. The residue was washed with cold water and then crystallized from 10 ml of water with carbon; a portion of the substance (a water-insoluble brown resin) remained on the filter. 0.15 g of white needles with m.p. 317-322° precipitated from the filtrate. A mixed specimen of both substances melted at 315-322°. The substance was crystallized twice from distilled water for analysis.

3.701 mg substance: 7.57 ml 0.01 N H_2SO_4. 3.761 mg substance: 7.63 ml 0.01 N H_2SO_4. Found %: N 28.63, 28.37. $C_8H_{10}O_2N_4$. Calculated %: N 28.86. Presence of OCH_3 not detected.

b) Preparation from 1,3-Dimethyl Uric Acid*. 0.5 g of 1,3-dimethyl uric acid, 5 ml of acetic anhydride and several drops of dimethylaniline were boiled on an oil bath for 80 hours. The transparent solution obtained evolved crystals on cooling to 0° which were drawn off and washed with ether. 0.3 g of white needles with m.p. 315-320° was obtained. The acetic anhydride was distilled off in a vacuum. The residue (0.15 g) was treated with ether and crystallized from 3 ml of water with carbon. White needles with m.p. 318-318.5° were obtained. A mixed sample of both substances with the substance obtained by method "a" melted at the same temperature.

c) Preparation from 1,3-Dimethyl-4-amino-5-acetylaminouracil (VII). 2.1 g of 1,3-dimethyl-4-amino-5-acetylaminouracil and 4 ml of 10% NaOH solution were stirred and heated on a water bath. The reaction mass became viscous, but dissolved as the heating was intensified. The reaction medium was alkaline to thymolphthalein. After 20 minutes of heating the transparent solution foamed and began to crystallize rapidly. The reaction was continued on a boiling water bath for 25 minutes more and then the solidifying mass was dissolved in hot water, filtered and the filtrate was acidified. 1.05 g of fine needles of a bright yellow substance with m.p. 315-316° thereupon separated out. A mixed specimen with 8-methyltheophylline obtained by methods "a" and "b" melted at 315-320°.

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* 1,3-Dimethyl uric acid was prepared by a method analogous to that described for the synthesis of unmethylated uric acid [4], i.e., via fusion of 1,3-dimethyl-4,5-diaminouracil with urea. Dimethyldiaminouracil was synthesized according to the directions of Bobranski and Synowiedski [5].

0.5 g of the substance was dissolved while being heated in 1.14 ml of 8% NaOH solution and 1.5 ml of water was added, and, in drops, during vigorous stirring, 0.25 ml of dimethylsulfate. The transparent solution gradually crystallized; pH 8-9. On heating on a water bath it all dissolved and crystallized again on cooling. The weight of the filtered and ice water-washed precipitate was 0.44 g and its m.p. 207-208°. The melting point of a mixed specimen with methylcaffeine was 207-208°.

1,3-Dimethyl-4-acetylmethylamino-5-diacetylaminouracil (XI)

1 g of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil (with m.p. 185°) and 20 ml of acetic anhydride were boiled for 40 hours. The material entirely dissolved. The acetic anhydride was distilled off in a vacuum, and the residue was stirred with ether and was drawn off. The weight was 1.16 g and the m.p. 175°. It was boiled with 20 ml of dry benzene. The substance dissolved and on cooling crystallized out in coarse elongated plates, intergrown with each other, with m.p. 179-181°. The melting point of a mixed specimen with the starting material was 157-167°, with methyl caffeine (m.p. 207-208°) was 166-178°.

The substance was dissolved in hot water (1: 6) and crystallized on cooling in the form of coarse polyhedral prisms. It crystallized from ethyl acetate as well as from benzene in the form of elongated transparent plates. It did not dissolve in a solution of alkali.

3.185 mg substance: 4.14 ml 0.01 N H_2SO_4. 4.251 mg substance: 5.51 ml 0.01 N H_2SO_4. 3.844 mg substance: 7.109 mg CO_2; 1.868 mg H_2O. 4.133 mg substance: 7.649 mg CO_2; 1.997 mg H_2O. Found %: N 18.20, 18.16; C 50.47, 50.50; H 5.42, 5.40. $C_{13}H_{18}O_5N_4$. Calculated %: N 18.06; C 50.32; H 5.8.

1,3,8,9-Tetramethylisoxanthine

3 g of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil (III) was boiled for 3 hours with 15 ml of 10% HCl, the last 20 minutes with carbon. It was filtered with water and the mixture of acids (acetic and hydrochloric) was distilled off in a vacuum. The dry residue was dissolved in a small quantity of water and neutralized with 10% NaOH solution. An abundant crystalline sediment precipitated. The weight was 1.84 g and the m.p. 252-254°. It crystallized from water (12: 100) in the form of fine needles, and from alcohol in the form of elongated plates. It was slightly soluble in boiling benzene, somewhat more soluble in ethyl acetate; it was moderately soluble in cold chloroform and more soluble on heating. M.p. 254°.

4.184 mg substance: 8.06 ml 0.01 N H_2SO_4. 3.621 mg substance: 6.89 ml 0.01 N H_2SO_4. 4.207 mg substance: 7.941 mg CO_2; 2.232 mg H_2O. 3.594 mg substance: 6.820 mg CO_2; 1.920 mg H_2O. Found %: N 26.97, 26.63; C 51.51, 51.79; H 5.94, 5.98. $C_9H_{12}O_2N_4$. Calculated %: N 26.92; C 51.92; H 5.77

SUMMARY

1. As a result of heating 4,5-di-(acetylamino)-uracil with dilute mineral acids, cyclization with formation of 8-methylxanthine proceeds along with hydrolysis of both acetyl groups.

2. Substitution of methyl groups for the mobile hydrogen atoms of the acetylamino group in 4,5-di-(acetylamino)-uracil stabilizes the bond of the acetyl groups with the nitrogen atom and thereby impedes their hydrolytic cleavage.

3. It was established that the trimethyl derivative of 4,5-di-(acetylamino)-uracil, obtained as a result of its methylation with dimethylsulfate, consists of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil. Heating it with dilute hydrochloric acid leads to the formation of 1,3,8,9-tetramethylisoxanthine (8-methylisocaffeine).

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SYNTHESIS OF DERIVATIVES OF PHENOTHIAZINE-1-CARBOXYLIC ACID

N. V. Savitskaya and M. N. Shchukina

The object of the present work was the synthesis of the amide and hydrazide of phenothiazine-1-carboxylic acid and a series of their derivatives for the study of their antibacterial action.

It is well known that phenothiazine has a distinct antituberculosis action in vitro [1]. It was of interest to examine how the introduction of such groups as the carbohydrazide and carbamide groups, the presence of which in compounds of the pyridine [2], pyrazine [3] and thiazole [4] series is associated with considerable antituberculosis activity, influenced the activity.

Although phenothiazine-1-carboxylic acid has been described in the literature in sufficient detail [5], the derivatives of interest to us had not been known and it turned out that certain difficulties were involved in their preparation. The formation of the amide of phenothiazine-1-carboxylic acid from its methyl ether did not proceed with aqueous ammonia either in the cold or during heating, and proceeded with alcoholic ammonia in an autoclave with only very small yields. A completely satisfactory yield of the amide was obtained by the reaction of the acid chloride of phenothiazine-1-carboxylic acid with gaseous ammonia. It turned out during the attempts to prepare the acid chloride of phenothiazine-1-carboxylic acid that during the action of excess thionylchloride and also during the action of a mixture of phosphoryl chloride and phosphorous pentachloride on the acid, there occurs not only formation of the acid chloride, but also substitution of the chlorine atom for three hydrogen atoms in the phenothiazine molecule. Under these circumstances the acid chloride of trichlorophenothiazine-1-carboxylic acid was obtained, from which the corresponding amide and diethylamide were obtained. The S-dioxide was prepared from the amide.

Boiling phenothiazine-1-carboxylic acid with phosphorous trichloride in benzene also failed to lead to the formation of the acid chloride of this acid, and it was only on heating it in a tube with excess phosphorous trichloride for 20 hours at 95° that the acid chloride was obtained in a yield of 75%. The preparation of the acid chloride by the action of phosphorous pentachloride in benzene on the acid at room temperature proved to be a more convenient method; in this case the reaction was completed in 10 minutes.

The p-anisidide, diethylamide and butylamide of phenothiazine-1-carboxylic acid were prepared by the action of the amines on a benzene solution of the acid chloride. The diethylamide and butylamide consisted of viscous non-crystalline substances. They were converted into the S-dioxides by boiling with hydrogen peroxide in glacial acetic acid.

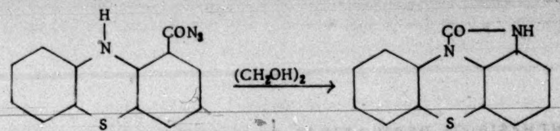
The synthesis of the hydrazide of phenothiazine-1-carboxylic acid was accomplished by boiling its amide with excess hydrazine hydrate for 20 hours.

By heating the hydrazide in alcoholic solution with, respectively, benzaldehyde, p-acetaminobenzaldehyde and p-hydroxybenzaldehyde, the corresponding hydrazones were obtained.

We attempted to utilize the Schmidt reaction to obtain 1-aminophenothiazine. We took chloroform as the solvent while 94 and 98% sulfuric acid was the catalyst; the temperature was varied within the range 30-50° and the quantity of sodium azide was varied from 1 to 1.5 moles, but a highly resinified phenothiazine-1-carboxylic acid was recovered in all cases.

The reaction of the hydrazide of phenothiazine-1-carboxylic acid with nitrous acid was also conducted. By boiling the azide obtained in absolute alcohol a difficultly-soluble, dark red substance was isolated which did not yield to purification and which was not converted into the amine either on boiling with concentrated hydrochloric acid or with alkali.

We succeeded in obtaining the azide of phenothiazine-1-carboxylic acid by the reaction of the acid chloride of the acid with sodium azide, and attempted to subject the acid to a Curtius rearrangement in an ethylene glycol medium with the object of converting it into an amine. However, a urethane was not obtained as a result of this reaction; rather, cyclization with formation of an imidazole ring proceeded:



A similar conversion has been described by Rodionov and Bezinger [6] for azides of N-benzoylated β-amino acids which, instead of the expected isocyanates very readily yield imidazole derivatives on simple heating in anhydrous solvents. Analyses of the substance and its properties – stability on heating with alkali, with concentrated hydrochloric acid, and in a mixture with glacial acetic acid – confirmed the imidazole structure of the compound obtained.

All the substances synthesized were investigated with reference to their antituberculosis activity.

The investigation demonstrated that not one of these substances possessed significant antituberculosis activity.

EXPERIMENTAL

Amide of Phenothiazine-1-carboxylic Acid

12 g of phosphorus pentachloride was added to a suspension of 10 g of phenothiazine-1-carboxylic acid in 400 ml of benzene and the mixture was stirred energetically at room temperature for 10 minutes. Almost all the acid went into solution, and the solution acquired a dark red color. Gaseous ammonia was passed into the solution until complete decolorization resulted, and 200 ml of water was then added; after some shaking the benzene layer was separated. The residue, after the benzene had been distilled off, was combined with the material obtained by filtering the aqueous layer and recrystallized twice from benzene. 5 g of the amide with a m.p. of 164-165.5° was obtained. It was a yellow crystalline powder, quite soluble in ether, dioxane, benzene, alcohol, ethyl acetate, and insoluble in water and petroleum ether.

4.431 mg substance: 0.466 ml N_2 (23.5°, 729 mm). Found % N 11.59. $C_{13}H_{10}ON_2S$. Calculated % N 11.57.

S-Dioxide of the Amide of Phenothiazine-1-carboxylic Acid

A mixture of 2 g of the amide of phenothiazine-1 carboxylic acid, 3 ml of a 27% aqueous solution of hydrogen peroxide and 30 ml of glacial acetic acid was heated to boiling for 5 hours. The reaction mass was then poured into 100 ml of cold water. An oily liquid then began to form and quickly crystallized into a light brown powder with a m.p. of 246-255°. The weight was 1.8 g. It recrystallized from alcohol as a white crystalline powder (needles) with a m.p. of 256-258°, quite soluble in alcohol, acetone, and insoluble in benzene, chloroform, ether and water.

3.940 mg substance: 8.201 mg CO_2; 1.304 mg H_2O. 7.438 mg substance: 5.26 ml 0.01 N H_2SO_4. Found %: C 56.80; H 3.70; N 9.90. $C_{13}H_{10}O_3N_2S$. Calculated %: C 56.93; H 3.65; N 10.22.

S-Dioxide of the Butylamide of Phenothiazine-1-carboxylic Acid

7 g of butylamine was added to a benzene solution of the acid chloride of phenothiazine-1-carboxylic acid obtained from 2.5 g of phenothiazine-1-carboxylic acid, 3 g of phosphorus pentachloride and 100 ml of benzene, and the mixture was left overnight. The reaction mass was then diluted with 75 ml of water and the benzene layer was separated while the water layer was extracted with benzene. After distilling off the benzene, 30 ml of glacial acetic acid and 6 ml of a 27% aqueous solution of hydrogen peroxide were added to the residue and the mixture was heated to boiling for 6 hours, after which the reaction mass was poured out into water and the S-dioxide of the butylamide of phenothiazine-1-carboxylic acid (3.1 g, m.p. 126-140°) which was formed was separated and recrystallized twice from benzene. The m.p. was 133.5-135°. It consisted of a white crystalline powder (needles), soluble in alcohol, acetone, chloroform, benzene and insoluble in water and petroleum ether.

3.451 mg substance: 7.752 mg CO_2; 1.650 mg H_2O. Found %: C 61.30; H 5.35. $C_{17}H_{18}O_3N_2S$. Calculated %: C 61.79; H 5.49.

S-Dioxide of the Diethylamide of Phenothiazine-1-carboxylic Acid

15 g of diethylamine was added to the benzene solution of the acid chloride of phenothiazine-1-carboxylic acid obtained from 5 g of phenothiazine-1-carboxylic acid, 6 g of phosphorus pentachloride and 200 ml of benzene, and the mixture was left overnight. The reaction mass was then diluted with 100 ml of water, acidified with hydro-

chloric acid and the benzene layer was separated while the aqueous layer was extracted once more with benzene. After elimination of the benzene the residue was vacuum distilled. A fraction with a b.p. of 220-225° at 0.75 mm was collected which consisted of a viscous, ductile mass. We dissolved this mass in 50 ml of glacial acetic acid and heated it to boiling for 6 hours with 10 ml of a 27% aqueous solution of hydrogen peroxide. On cooling, the S-dioxide of the diethylamide of phenothiazine-1-carboxylic acid with a m.p. of 170-174° was isolated; after recrystallization from alcohol, it had a m.p. of 175-178°. It was a white crystalline powder, quite soluble in alcohol, benzene, chloroform and insoluble in ether.

3.411 mg substance: 7.702 mg CO_2; 1.627 mg H_2O. Found %: C 61.62; H 5.34. $C_{17}H_{18}O_3N_2S$. Calculated %: C 61.79; H 5.45.

p-Anisidide of Phenothiazine-1-carboxylic Acid

1.5 g of p-anisidine was added to a benzene solution of phenothiazine-1-carboxylic acid, prepared from 1 g of phenothiazine-1-carboxylic acid, 1.2 g of phosphorus pentachloride and 40 ml of benzene. Vigorous evolution of heat thereupon occurred, the color of the solution changed, and a yellow-green precipitate began to settle out which was separated and washed with water. After washing the benzene layer with water and eliminating the benzene, a yellow-green residue was also obtained which was added to the other precipitate. The yield was 1.3 g and the m.p. was 208-211°. It melted at 210-212° after recrystallization from isopropyl alcohol. It was a yellow-green crystalline powder, quite soluble in alcohol, acetone, benzene and insoluble in ether and water.

3.910 g substance: 9.871 mg CO_2; 1.508 mg H_2O. Found %: C 68.90; H 4.32. $C_{20}H_{16}O_2N_2S$. Calculated %: C 68.93; H 4.59.

Hydrazide of Phenothiazine-1-carboxylic Acid

A mixture of 3.9 g of the amide of phenothiazine-1-carboxylic acid and 5 g of hydrazine hydrate was heated to boiling for 20 hours after which the solid mass was recrystallized from alcohol. 3.2 g of the hydrazide with a m. p. of 143-145° was obtained. After recrystallization from benzene the m.p. was 145.5-147°. It consisted of yellow-green needles, quite soluble in alcohol, ether, benzene, acetone, dichloroethane and insoluble in petroleum ether and water.

2.380 mg substance: 0.340 ml N_2 (19°, 738 mm). Found %: N 16.21. $C_{13}H_{11}ON_3S$. Calculated %: N 16.34.

N^2-Benzalhydrazide of Phenothiazine-1-carboxylic Acid

A solution of 1.8 g of the hydrazide of phenothiazine-1-carboxylic acid in 7 ml of alcohol was heated to boiling for 20 minutes with 1 g of benzaldehyde.

After cooling the solution, an orange crystalline powder was isolated which melted at 221-223° after recrystallization from alcohol.

3.700 mg substance: 9.390 mg CO_2; 1.430 mg H_2O. Found %: C 69.26; H 4.32. $C_{20}H_{15}ON_3S$. Calculated %: C 69.54; H 4.35.

N^2-p-Acetaminobenzalhydrazide of Phenothiazine-1-carboxylic Acid

1.5 g of p-acetaminobenzaldehyde in 5 ml of alcohol was added to 1.5 g of the hydrazide of phenothiazine-1-carboxylic acid in 10 ml of alcohol, and the mixture was heated to boiling for 20 minutes. The orange precipitate (weight 2.1 g, m.p. 254-262°) which crystallized after cooling was separated and recrystallized twice from glacial acetic acid; m.p. 264-266°. The substance was difficultly soluble in the ordinary organic solvents.

3.426 mg substance: 8.227 mg CO_2; 1.407 mg H_2O. Found %: C 65.53; H 4.60. $C_{22}H_{18}O_2N_4S$. Calculated %: C 65.67; H 4.47.

N^2-p-Hydroxybenzalhydrazide of Phenothiazine-1-carboxylic Acid

A mixture consisting of 1.5 g of the hydrazide of phenothiazine-1-carboxylic acid and 1 g of p-hydroxybenzaldehyde in 15 ml of alcohol was heated to boiling for 40 minutes and left overnight. 2.15 g of substance with a m.p. of 219-225° was obtained after filtration which, after two recrystallizations from aqueous alcohol, had a m.p. of 242-244°. It consisted of an orange powder, quite soluble in alcohol, acetone, ethyl acetate and insoluble in petroleum ether and water.

4.780 mg substance: 11.649 mg CO_2; 1.810 mg H_2O. 5.930 mg substance: 0.620 ml N_2 (23°, 726 mm). Found %: C 66.50; H 4.23; N 11.52 $C_{20}H_{15}O_2N_3S$. Calculated % C 66.46; H 4.15; N 11.63.

Acid Chloride of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 1.8 g of phenothiazine-1-carboxylic acid and 10 ml of thionyl chloride was heated to boiling for 3 hours. Excess thionyl chloride was distilled off from the reaction mass, and the residue was washed with ether and recrystallized twice from dichloroethane; m.p. 219-220°. The substance was dark red in color and difficultly soluble in the ordinary organic solvents.

5.788 mg substance: 9.075 mg AgCl. Found %: Cl 38.79. $C_{13}H_5ONSCl_4$. Calculated %: Cl 38.87.

Amide of Trichlorophenothiazine-1-carboxylic Acid

Gaseous ammonia was passed into a benzene solution of 1 g of the acid chloride of trichlorophenothiazine-1-carboxylic acid until the red coloration disappeared. The yellow crystalline substance which separated was filtered off and washed with water. After having been recrystallized twice from alcohol, it melted with decomposition at 288°.

5.040 mg substance: 6.377 mg AgCl. Found %: Cl 31.30. $C_{13}H_7ON_2SCl_3$. Calculated %: Cl 30.79.

S-Dioxide of the Amide of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 0.5 g of the amide of trichlorophenothiazine-1-carboxylic acid, 25 ml of glacial acetic acid and 4 ml of a 27% aqueous solution of hydrogen peroxide was heated to boiling for 1 hour and then left overnight. The slightly yellowish crystals which settled out were separated and recrystallized from glacial acetic acid.

4.717 mg substance: 5.360 mg AgCl. 4.942 mg substance: 0.321 ml N_2 (21°, 736 mm). Found %: Cl 28.11; N 7.31. $C_{13}H_7O_3N_2SCl_3$. Calculated %: Cl 28.18; N 7.42.

Diethylamide of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 1.4 g of the acid chloride of trichlorophenothiazine-1-carboxylic acid, 0.8 g of diethylamine and 20 ml of acetone was heated to boiling for 5 hours. After distilling off the acetone, a yellowish precipitate with a m.p. of 107-109.5° separated out which was quite soluble in alcohol and in benzene. After it had been recrystallized twice from 70% alcohol, the m.p. was 110.5-111.5°.

5.881 mg substance: 0.351 ml N_2 (18°, 742 mm). 3.721 mg substance: 3.940 mg AgCl. Found %: N 6.83; Cl 26.20. $C_{17}H_{15}N_2OSCl_3$. Calculated %: N 6.97; Cl 26.49.

Acid Chloride of Phenothiazine-1-carboxylic Acid

A mixture consisting of 4 g of phenothiazine-1-carboxylic acid and 10 ml of phosphorus trichloride was heated in a sealed tube at 100° for 20 hours. The phosphorus trichloride was distilled off, the acid chloride was washed with ether, dried in a vacuum desiccator and subjected to further treatment without purification. The weight was 3.5 g.

Azide of Phenothiazine-1-carboxylic Acid

A solution of 3 g of the acid chloride of phenothiazine-1-carboxylic acid in 120 ml of dry dioxane was cooled to 20° and a solution of 2 g of sodium azide in 5 ml of water was added to it in one dose. After standing for 10 minutes, the azide was precipitated by water in the form of a light red powder which was collected, dried and subjected to further treatment without purification. The weight was 3 g.

Phenothiazimidazolone

A suspension of 2.5 g of the azide of phenothiazine-1-carboxylic acid in 20 ml of ethylene glycol was heated on an oil bath, initially at a temperature of 110-120° until nitrogen evolution ceased, and then for 30 minutes at 140-150°. The reaction mass was poured into a large quantity of water, the yellow crystalline substance which precipitated was collected, dried (weight 3 g) and recrystallized twice from glacial acetic acid and then from alcohol. After the three recrystallizations, the phenothiazimidazolone consisted of a colorless crystalline substance with a m.p. of 289-290° which did not change during prolonged boiling with alkalis, with concentrated hydrochloric acid and in a mixture with glacial acetic acid.

4.748 mg substance: 11.280 mg CO_2; 1.419 mg H_2O. 3.730 mg substance: 8.845 mg CO_2; 1.099 mg H_2O. 5.050 mg substance: 0.523 ml N_2 (25°, 744 mm). Found %: C 64.83, 64.71; H 3.34, 3.3; N 11.61. $C_{13}H_8ON_2S$. Calculated %: C 65.00; H 3.33; N 11.66.

SUMMARY

1. The following were synthesized: a) the amide of phenothiazine-1-carboxylic acid, its S-dioxide, the S-dioxides of the butylamide and diethylamide and the p-anisidide of phenothiazine-1-carboxylic acid; b) the hydrazide of phenothiazine-1-carboxylic acid and from it, the corresponding hydrazones, were synthesized with benzaldehyde, p-acetaminobenzaldehyde and with p-hydroxybenzaldehyde.

2. It was demonstrated that during the action on phenothiazine-1-carboxylic acid of excess thionyl chloride or a mixture of phosphoryl chloride and phosphorus pentachloride, the substitution of three hydrogen atoms in the molecule by chlorine occurs. The acid chloride of trichlorophenothiazine-1-carboxylic acid, its amide, diethylamide and the S-dioxide of the amide were prepared.

3. It was proved that when the Curtius rearrangement of the azide of phenothiazine-1-carboxylic acid is conducted, the formation of an imidazole ring occurs.

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All-Union Scientific Research
Chemico-Pharmaceutical Institute

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* See Consultants Bureau Translation, page 847.

SUMMARY

2. The following [illegible]

3. It was demonstrated that during the [illegible] of phosphoryl chloride and phosphorus pentachloride, the substitution of the [illegible] atoms in the molecule by chlorine occurs. [illegible] and the S-[illegible] of the [illegible] were prepared.

4. It was proved that when the [illegible] is conducted, the formation of [illegible]

LITERATURE CITED

(1) C. F. Hamilton, [illegible]

(2) M. [illegible]

(3) [illegible]

(4) [illegible]

(5) [illegible]

(6) V. M. [illegible]

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* See Consultants Bureau Translation, page [illegible]

ACETYLENE DERIVATIVES. 165.

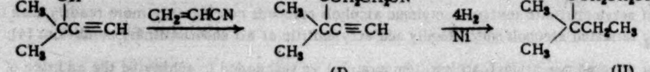
CYANETHYLATION OF ACETYLENIC ALCOHOLS AND GLYCOLS

I. N. Nazarov and G. A. Shvekhgeimer

While the addition of acrylonitrile to saturated alcohols and glycols has been well studied [1], the addition of acrylonitrile to acetylenic alcohols and glycols, with the exception of isolated patents [2] has not been described in the literature. In particular, the addition of acrylonitrile to acetylenic glycols has not been investigated at all, although such glycols are readily available and compounds formed from them by the addition of acrylonitrile can be of interest as intermediate products in the preparation of other valuable substances.

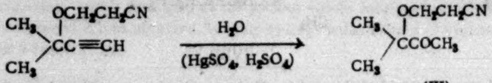
We conducted all the reactions involving the addition of acrylonitrile to unsaturated alcohols and glycols in the presence of a 40% aqueous solution of potassium hydroxide.

During the addition of acrylonitrile to dimethylethynylcarbinol, the β-cyanethyl ether (I) was obtained in a yield of 84%, which on hydrogenation in an autoclave in the presence of Ni catalyst added 4 molecules of hydrogen and yielded the γ-aminopropyl ether of dimethylethylcarbinol (II) in 91% yield:



(I) (II)

The β-cyanethyl ether of dimethylacetylcarbinol (III) was obtained in a yield of 79% by the hydration of the β-cyanethyl ether of dimethylethynylcarbinol (I) in water-dioxane in the presence of mercuric sulfate and sulfuric acid:

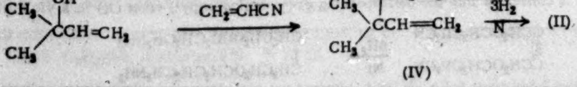


(III)

In the presence of mercuric sulfate alone (without sulfuric acid), the indicated hydration leads to the formation of the β-cyanethyl ether (III) in a yield of only 24%.

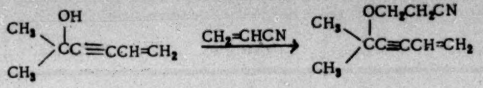
The β-cyanethyl ether (IV) in a yield of 95%, calculating on the basis of the amount of carbinol entering into the reaction, was formed by the action of acrylonitrile on dimethylvinylcarbinol. At the same time, a considerable portion of the unreacted carbinol was recovered.

The γ-aminopropyl ether of dimethylethylcarbinol (II) described above was obtained by the hydrogenation of the β-cyanethyl ether of dimethylvinylcarbinol (IV) in an autoclave.



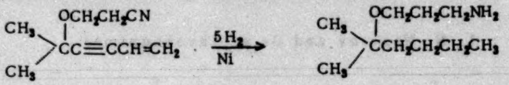
(IV)

Dimethylvinylethynylcarbinol readily adds a molecule of acrylonitrile in the presence of a 40% aqueous solution of potassium hydroxide and forms the β-cyanethyl ether (V) in a yield of 79%:



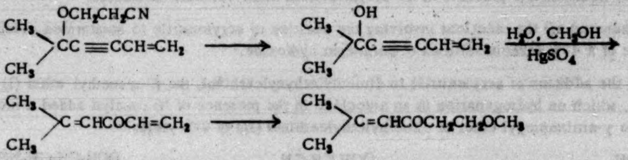
(V)

The β-cyanethyl ether (V) rapidly polymerizes on standing into a transparent yellow colored jelly. The γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained in a yield of 94% by the hydrogenation of the β-cyanethyl ether (V) in an autoclave in the presence of Ni catalyst:



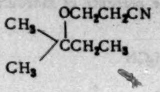
(VI)

At attempt to hydrogenate the β-cyanethyl ether (V) in a water-methanol medium led to the elimination of a molecule of acrylonitrile with subsequent isomerization of the dimethylvinylethynylcarbinol which was formed into β,β dimethyldivinylketone, the latter added methanol under the conditions of the reaction and was converted into 1-methoxy-5-methyl-4-hexen-3-one [3].

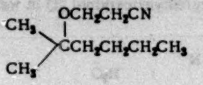


The addition of acrylonitrile to tertiary acetylenic alcohols proceeds considerably more readily than to the corresponding tertiary saturated alcohols which hardly add acrylonitrile at all under ordinary conditions [4].

However, under selected conditions (catalyst, temperature) we succeeded in achieving the addition of acrylonitrile to dimethylethylcarbinol and dimethylbutylcarbinol and in obtaining the corresponding β-cyanethyl ethers (VII) and (VIII) in yields up to 50% (of the carbinol entering into the reaction):



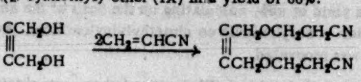
(VII)



(VIII)

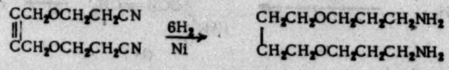
A great part of the carbinol was recovered unchanged in all these experiments. The above described γ-aminopropyl ethers (II) and (VI) are formed during the hydrogenation of the β-cyanethyl ethers (VII) and VIII).

The simplest acetylenic glycol – 1,4-butynediol – smoothly adds two molecules of acrylonitrile in dioxane solution and forms the di-(β-cyanethyl) ether (IX) in a yield of 88%:



(IX)

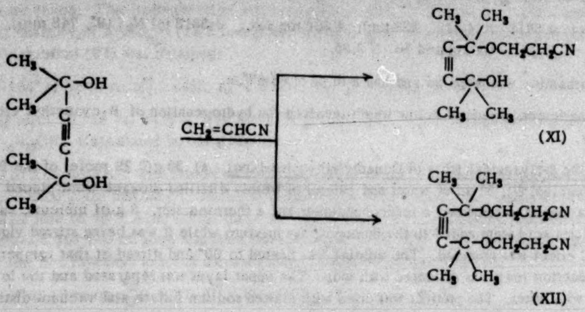
In the presence of Raney nickel at 100-110° in an autoclave the di-(β-cyanethyl) ether (IX) rapidly absorbs 6 molecules of hydrogen and is converted into the corresponding di-(γ-aminopropyl) ether (X) in a yield of 84%.



(X)

The hydration of compound (IX) in a water-dioxane medium led to the production of a small quantity of low boiling decomposition products, but the greater portion of the substance resinified.

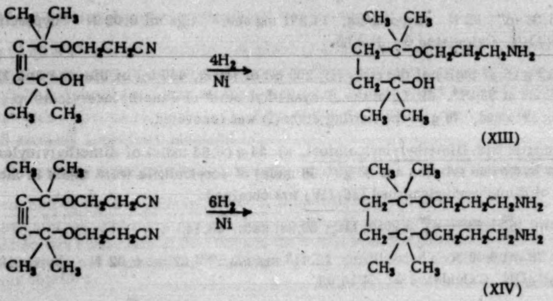
The addition of acrylonitrile to the ditertiary acetylenic glycol — tetramethylbutynediol — in dioxane solution requires heating the reaction mixture at 60-75° for 6 hours. A mixture of the mono- and di-(β-cyanethyl) ethers (XI) and (XIII) in approximately identical quantities was obtained as a result:



(XI)

(XII)

The saturated γ-aminopropyl ethers (XIII) and (XIV) were obtained in excellent yields by the hydrogenation of the ethers (XI) and (XII) in an autoclave at 100-110° over Raney nickel:



(XIII)

(XIV)

The β-cyanethyl ethers described in the present article consist of colorless liquids with a characteristic odor while the γ-aminopropyl ethers obtained by their hydrogenation consist of hygroscopic liquids with a characteristic amine odor which fume in air.

EXPERIMENTAL

Reaction of Acrylonitrile with Dimethylethynylcarbinol. 42 g (0.5 mole) of dimethylethynylcarbinol and 3 g of a 40% aqueous solution of potassium hydroxide were mixed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 26.5 g (0.5 mole) of acrylonitrile was gradually added in the course of one hour while the mixture was being stirred energetically. The temperature of the mixture was maintained below 35° by cooling with cold water. After the addition of the acrylonitrile the mixture was stirred at room temperature for 6 hours and then left overnight. On the next day the alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off and the filtrate was vacuum distilled. 57.5 g of the β-cyanethylester of dimethylethynylcarbinol (I) [2b] was obtained:

b.p. 96-96.5° at 18 mm; n_D^{20} 1.4356; d_4^{20} 0.9275; MR_D 38.52; calc. 38.54.

13.599 mg sub.: 5.05 ml 0.02 N hyposulfite; 13.816 mg sub.: 5.21 ml 0.02 N hyposulfite. Found %: N 10.30, 10.45. $C_8H_{11}ON$. Calculated %: N 10.22.

The addition of acrylonitrile was conducted analogously in all the other reactions described below.

Hydrogenation of the β-Cyanethyl Ether of Dimethylethynylcarbinol. 25 g (0.182 mole) of the β-cyanethyl ether of dimethylethynylcarbinol (I), 95 ml of methanol saturated with dry ammonia and 25 g of Raney nickel were placed in a 250 ml rotary autoclave. The hydrogenation was conducted for 1 hour 10 minutes at 100-110° and the initial pressure of the hydrogen was 140 atm. The theoretical quantity of hydrogen (16.5 liters) was absorbed. After the mixture had been cooled, the nickel was filtered off and the filtrate vacuum distilled. 24.2 g of the γ-aminopropyl ether of dimethylethylcarbinol (II) was obtained:

b.p. 68-70° at 14 mm; n_D^{20} 1.4360; d_4^{20} 0.8589; MR_D 44.14; calc. 44.21.

4.505 mg sub.: 0.3715 ml N_2 (19°, 738mm). 4.560 mg sub.: 0.3813 ml N_2 (19°, 748 mm). Found %: N 9.37, 9.44. $C_8H_{19}ON$. Calculated %: N 9.65.

The phenylcarbamide was prepared and had a m.p. of 66-67°.

The other experiments described below which involved the hydrogenation of β-cyanethyl ethers were conducted in a similar manner.

Hydration of the β-Cyanethyl Ether of Dimethylethynylcarbinol. a) 30 g (0.22 mole) of the β-cyanethyl ether of dimethylethynylcarbinol (I), 50 ml of water and 100 ml of freshly distilled dioxane were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. 3 g of mercuric sulfate and 2 drops of concentrated sulfuric acid were added to the homogeneous mixture while it was being stirred vigorously. No appreciable thermal effect was observed. The mixture was heated to 90° and stirred at that temperature for 6 hours. After cooling, the reaction mass was saturated with soda. The upper layer was separated and the lower layer was extracted three times with ether. The product was dried with roasted sodium sulfate and vacuum distilled after distilling off the solvent. 26.8 g of the β-cyanethyl ether of dimethylacetylcarbinol (III) was obtained:

b.p. 132-136° at 18 mm; n_D^{20} 1.4357; d_4^{20} 1.0033; MR_D 40.37; calc. 40.61.

16.217 mg sub.: 5.36 ml 0.02 N hyposulfite. 14.271 mg sub.: 4.78 ml 0.02 N hyposulfite. Found %: N 9.22, 9.27. $C_8H_{13}O_2N$. Calculated %: N 9.03.

b) A mixture of 119 g (9.87 mole) of the ether (I), 200 ml of water, 400 ml of dioxane and 12 g of mercuric sulfate was stirred for 6 hours at 90-91°. 32.3 g of the β-cyanethyl ether of dimethylacetylcarbinol (III) with a b.p. of 130-134° at 17 mm was obtained. 76 g of the starting ether (I) was recovered.

Reaction of Acrylonitrile with Dimethylvinylcarbinol. a) 54 g (0.63 mole) of dimethylvinylcarbinol, 3.5 g of 40% aqueous potassium hydroxide solution and 35 g (0.66 mole) of acrylonitrile were taken in the reaction. 32.5 g of the β-cyanethyl ether of dimethylvinylcarbinol [16] (IV) was obtained:

b.p. 94-96° at 16 mm; n_D^{20} 1.4337; d_4^{20} 0.9056; MR_D 39.98; calc. 40.14.

12.756 mg sub.: 4.79 ml 0.02 N hyposulfite. 12.448 mg sub.: 4.62 ml 0.02 N hyposulfite. Found %: N 10.39, 10.28. $C_8H_{13}ON$. Calculated %: N 10.08.

33 g of the starting carbinol was recovered. The yield of β-cyanethyl ether (IV) was 95%, calculated on the basis of the carbinol which reacted.

b) Reactants: 42 g (0.5 mole) of dimethylvinylcarbinol, 0.6 g of metallic sodium and 26.5 g (0.5 mole) of acrylonitrile. 43.2 g of the ether (IV) with a b.p. of 98-100° at 24 mm; n_D^{20} 1.4335, was obtained. 8 g of the starting dimethylvinylcarbinol was recovered. The yield of the β-cyanethyl ether (IV) was 78%, calculating on the basis of the carbinol which entered into the reaction.

Hydrogenation of the β-Cyanethyl Ether of Dimethylvinylcarbinol. 21 g (0.151 mole) of the β-cyanethyl ether of dimethylvinylcarbinol (IV), 95 ml of methanol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was conducted for 1 hour 45 minutes at 100-110° and the initial hydrogen pressure was 110 atm. The theoretical quantity of hydrogen (10.2 liters) was absorbed.

20.5 g of the above described γ-aminopropyl ether of dimethylethylcarbinol (II) with a b.p. of 56-58° at 7 mm; n_D^{20} 1.4338 was obtained.

The phenylcarbamide was prepared and had a m.p. of 66.5-67°.

Reaction of Acrylonitrile with Dimethylvinylethynylcarbinol. 165 g (1.5 mole) of dimethylvinylethynylcarbinol 10 g of 40% aqueous potassium hydroxide and 53 g (1 mole) of acrylonitrile were taken in the reaction. 129.5 g of the β-cyanethyl ether of dimethylvinylethynylcarbinol was obtained:

b.p. 93-94° at 6 mm; n_D^{20} 1.4710; d_4^{20} 0.9334; MR_D 48.81; calc. 47.31; EMR_D 1.50.

5.345 mg sub.: 0.4038 ml N_2 (20°, 728 mm). 4.235 mg sub.: 0.3293 ml N_2 (20°, 728 mm). Found %: N 8.44, 8.67. $C_{10}H_{13}ON$. Calculated %: N 8.59.

66.5 g of the starting dimethylvinylethynylcarbinol was recovered.

Hydrogenation of the β-Cyanethyl Ether of Dimethylvinylethynylcarbinol. 20 g (0.123 mole) of the β-cyanethyl ether of dimethylvinylethynylcarbinol (V), 105 ml of methyl alcohol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-110° and the initial hydrogen pressure was 135 atm. The theoretical quantity of hydrogen (13.8 liters) was absorbed after 30 minutes. 20.1 g of the γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained:

b.p. 102-104° at 18 mm; n_D^{20} 1.4485; d_4^{20} 0.8630; MR_D 53.71; calc. 53.44.

2.913 mg sub.: 0.216 ml N_2 (23°, 748 mm). 3.427 mg sub.: 0.255 ml N_2 (23°, 748 mm). Found %: N 8.42, 8.44. $C_{10}H_{23}ON$. Calculated %: N 8.09;

Reaction of Acrylonitrile with Dimethylethylcarbinol. a) 88 g (1 mole) of dimethylethylcarbinol, 2 g of powdered sodium methylate and 53 g (1 mole) of acrylonitrile were taken in the reaction. The temperature of the mixture gradually rose to 40°. After cessation of the evolution of heat, the stirring was continued for 4 hours more at room temperature and the mixture was then left overnight. The alkali was neutralized with hydrochloric acid (1:1). 14 g of the β-cyanethyl ether of dimethylethylcarbinol (VII) was obtained:

b.p. 92-97° at 18 mm; n_D^{20} 1.4247; d_4^{20} 0.8981; MR_D 40.12; calc. 40.60.

7.135 mg sub.: 2.61 ml 0.02 N hyposulfite. 13.318 mg sub.: 4.97 ml 0.02 N hyposulfite. Found %: N 10.13, 10.19. $C_8H_{15}ON$. Calculated %: N 9.94.

72.5 g of the starting dimethylethylcarbinol was recovered.

b) 35 g (0.66 mole) of acrylonitrile was added to a mixture of 57 g (0.04 mole) of dimethylethylcarbinol and 4 g of a 40% aqueous solution of potassium hydroxide. No appreciable thermal effect was observed. The mixture was heated to 80° and stirred for 1 hour at this temperature. The reaction mass was cooled after this and the alkali was neutralized with hydrochloric acid (1:1). 3.6 g of the β-cyanethyl ether of dimethylethylcarbinol with a b.p. of 92-97° at 18 mm; n_D^{20} 1.4247 was obtained.

44 g of the starting dimethylethylcarbinol was recovered.

Hydrogenation of the β-cyanethyl Ether of Dimethylethylcarbinol. 8.8 g (0.063 mole) of the β-cyanethyl ether of dimethylethylcarbinol, 120 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 95-105° and the initial hydrogen pressure was 120 atm. The theoretical quantity of hydrogen (2.8 liters) was absorbed in 30 minutes. 8.1 g of the above described γ-aminopropyl ether of dimethylethylcarbinol (II) was obtained:

b.p. 56-58° at 7 mm; n_D^{20} 1.4325.

4.271 mg sub.: 0.3538 ml N_2 (21°, 742 mm). 2.268 mg sub.: 0.1929 ml N_2 (21°, 742 mm). Found %: N 9.39, 9.64. $C_8H_{19}ON$. Calculated %: N 9.65.

The phenylcarbamide was prepared and had a m.p. of 66-67°.

Reaction of Acrylonitrile with Dimethylbutylcarbinol. a) 1.5 g of metallic potassium was added to 120 g (0.71 mole) of dimethylbutylcarbinol. After all the potassium had dissolved, 53 g (1 mole) of acrylonitrile was added to the mixture while it was being stirred vigorously and cooled with cold water. In the course of 2 hours the temperature gradually rose to 45° and then fell to 25°. The alkali was then neutralized with hydrochloric acid (1:1). 24.3 g of the β-cyanethyl ether of dimethylbutylcarbinol (VIII): was obtained:

b.p. 105-107° at 11 mm; n_D^{20} 1.4306; d_4^{20} 0.8825; MR_D 49.55; calc. 49.84.

b) 85 g (1.6 mole) of acrylonitrile was added to a mixture of 180 g (1.55 mole) of dimethylbutylcarbinol and 12 g of 40% aqueous potassium hydroxide while the mixture was being vigorously stirred. No thermal effect was observed. The mixture was heated to 70° and stirred at this temperature for 2 hours. After cooling, the alkali was neutralized with hydrochloric acid (1:1) and the mixture was treated in the usual manner. 18 g of the β-cyanethyl ether of dimethylbutylcarbinol was obtained:

b.p. 102-105° at 10 mm; n_D^{20} 1.4308; d_4^{20} 0.8826; MR_D 49.54; calc. 49.84.

4.640 mg sub.: 0.3352 ml N_2 (20°, 724 mm). 3.665 mg sub.: 0.2666 ml N_2 (20°, 731 mm). Found %: N 8.01, 8.00. $C_{10}H_{19}ON$. Calculated %: N 9.28.

155.5 g of the starting carbinol was recovered.

Hydrogenation of the β-Cyanethyl Ether of Dimethylbutylcarbinol. 29 g (0.172 mole) of the β-cyanethyl ether of dimethylbutylcarbinol, 120 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 85-95° and the initial hydrogen pressure was 120 atm. The theoretical quantity of hydrogen (7.7 liters) was absorbed in 40 minutes. 27.6 g of the above described γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained:

b.p. 78-81° at 6 mm; n_D^{20} 1.4482.

3.125 mg sub.: 0.228 ml N_2 (23°, 748 mm). 3.536 mg sub.: 0.257 ml N_2 (23°, 748 mm). Found %: N 8.28, 8.25. $C_{10}H_{23}ON$. Calculated %: N 8.09.

Reaction of Acrylonitrile with 1,4-Butynediol. 125 g (2.36 mole) of acrylonitrile was gradually added to a mixture of 101 g (1.174 mole) 1,4-butynediol, 150 ml of freshly distilled dioxane and 7 g of a 40% aqueous solution of potassium hydroxide while the mixture was vigorously stirred and cooled with cold water, at such a rate that the temperature of the mixture did not rise above 35°. The stirring was continued at room temperature for 4 hours after the addition of the acrylonitrile and the mixture was then left for 48 hours. The alkali was neutralized with concentrated hydrochloric acid and the product was treated in the usual manner. 216 g of the di-(β-cyanethyl) ether of 1,4-butynediol was obtained in the form of a light yellow viscous oil:

b.p. 189-195° at 3 mm; n_D^{20} 1.4760; d_4^{20} 1.0910; MR_D 49.29; calc. 49.24.

13.541 mg sub.: 5.90 ml 0.02 N hyposulfite. 12.274 mg sub.: 6.16 ml 0.02 N hyposulfite. Found %: N 14.45, 14.43. $C_{10}H_{12}O_2N_2$. Calculated %: N 14.56.

Hydrogenation of the Di-(β-cyanethyl) Ether of 1,4-Butynediol. 19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,4-butynediol (IX), 90 ml of methyl alcohol saturated with dry ammonia and 2.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-105° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in 20 minutes. 17.5 g of the di-(γ-aminopropyl) ether of 1,4-butanediol (X) was obtained:

b.p. 134-136° at 4 mm; n_D^{20} 1.4618; d_4^{20} 0.9620; MR_D 58.59; calc. 58.51.

12.317 mg sub.: 1.143 ml N_2 (22°, 757 mm). 9.636 mg sub.: 1.126 ml N_2 (22°, 757 mm). Found %: N 13.63, 13.44. $C_{10}H_{24}O_2N_2$. Calculated %: N 13.72.

Reaction of Acrylonitrile with Tetramethylbutynediol. 50 g (0.94 mole) of acrylonitrile was added to a mixture of 59 g (0.415 mole) of tetramethylbutynediol, 200 ml of freshly distilled dioxane and 4 g of a 40% aqueous solution of potassium hydroxide while the mixture was vigorously stirred. No thermal effect was observed. The mixture was stirred for 5 hours at 60-70° and for one hour at 70-75°, after which it was left to stand for 40 hours. The alkali was neutralized with concentrated hydrochloric acid and the product was treated in the usual manner The following fractions were obtained after fivefold vacuum distillation: 1) 111-112° at 3 mm (37.6 g), 2) 112-132° at 2.5 mm (7.9 g), 3) 142-146° at 2.5 mm (32.1 g).

The first fraction consisted of the mono-β-cyanethyl ether of tetramethylbutynediol (XI):

b.p. 111-112° at 3 mm; n_D^{20} 1.4530; d_4^{20} 0.9758; MR_D 54.01; calc. 53.92.

9.45 mg sub.: 23.44 mg CO_2; 7.65 mg H_2O. 10.19 mg sub.: 25.42 mg CO_2; 8.05 mg H_2O. Found %: C 67.70, 67.92; H 9.05, 8.84. $C_{11}H_{17}O_2N$. Calculated %: C 67.69; H 8.72.

The third fraction consisted of the di-(β-cyanethyl) ether of tetramethylbutynediol (XII); it was a colorless viscous liquid which crystallized on standing:

b.p. 142-146° at 2.5 mm; m.p. about 25°; n_D^{20} 1.4553; d_4^{20} 0.9915; MR_D 67.91; calc. 67.71.

5.795 mg sub.: 14.285 mg CO_2; 4.230 mg H_2O. 5.515 mg sub.: 13.567 mg CO_2; 3.890 mg H_2O. Found %: C 67.27, 67.13; H 8.17, 7.89. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.74; H 8.07.

Hydrogenation of the Mono-β-cyanethyl Ether of Tetramethylbutynediol. 19.5 g (0.1 mole) of the mono-β-cyanethyl ether of tetramethylbutynediol (XI), 100 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed in one hour. 18 g of the mono-γ-aminopropyl ether of tetramethylbutanediol was obtained:

b.p. 91-94° at 4 mm; n_D^{20} 1.4587; d_4^{20} 0.9321; MR_D 59.50; calc. 59.59.

4.850 mg sub.: 0.2936 ml N_2 (21°, 726 mm). 3.910 mg sub.: 0.2411 ml N_2 (21°, 726 mm). Found %: N 6.71, 6.86. $C_{11}H_{23}O_2N$. Calculated %: N 6.89.

The phenylcarbamide was prepared and had a m.p. of 181.5-182.5°.

Hydrogenation of the Di-(β-cyanethyl) Ether of Tetramethylbutynediol. 24.8 g (0.1 mole) of the di-(β-cyanethyl) ether of tetramethylbutynediol (XII), 90 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90 100° and an initial hydrogen pressure of 135 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in one hour. 21 g of the di-(γ-aminopropyl) ether of tetramethylbutanediol (XIV) was obtained:

b.p. 136-138° at 3.5 mm; n_D^{20} 1.4752; d_4^{20} 0.9539; MR_D 76.77; calc. 76.98.

12.725 mg sub.: 5.60 ml 0.02 N hyposulfite. 12.968 mg sub.: 5.72 ml 0.02 N hyposulfite. Found %: N 10.95, 10.95. $C_{14}H_{32}O_2N_2$. Calculated %: N 10.77.

The phenylcarbamide was prepared and had a m.p. of 115-116° (from alcohol).

SUMMARY

1. The addition of acrylonitrile to dimethylethynylcarbinol, dimethylvinylcarbinol, dimethylvinylethynylcarbinol, 1,4 butynediol, tetramethylbutynediol and the preparation of the corresponding β nitrilethyl ethers in high yields was described.

2. The possibility of adding acrylonitrile to tertiary saturated alcohols under ordinary conditions was demonstrated.

3. The corresponding γ-aminopropyl ethers were obtained in high yields by the hydrogenation of the β-cyanethyl ethers.

4. The β-cyanethyl ether of dimethylethynylcarbinol formed the β-cyanethyl ether of dimethylacetylcarbinol in a yield of 79% during hydration in the presence of mercuric sulfate and sulfuric acid.

5. Attempts to hydrate the β-cyanethyl ethers of dimethylvinylethynylcarbinol and 1,4-butynediol were not successful.

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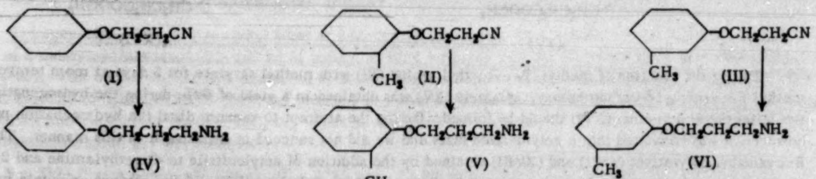
THE CYANETHYLATION OF CYCLIC AND HETEROCYCLIC ALCOHOLS AND AMINES.

HYDROGENATION AND ALCOHOLYSIS OF THE CYANETHYLATION PRODUCTS

I. N. Nazarov and G. A. Shvekhgeimer

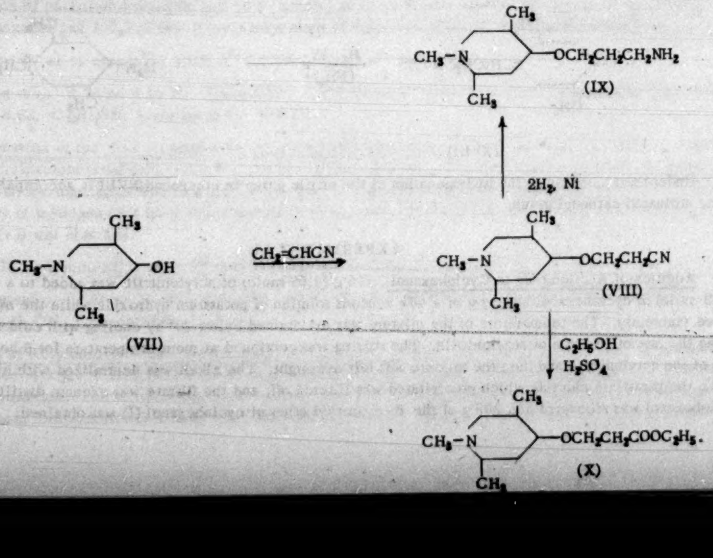
The addition of acrylonitrile to cyclic and heterocyclic alcohols has hardly been investigated at all until recently. In particular, data concerning the addition of acrylonitrile to alcohols of the cyclohexanol series are almost entirely absent in the literature. The addition of acrylonitrile to γ-piperidols, which are important starting materials for the synthesis of physiologically active compounds, has not been studied at all.

The addition of acrylonitrile to cyclohexanol, 2- and 3-methylcyclohexanols, 1,2,5-trimethyl-4-piperidol and also the hydrogenation and alcoholysis of the compounds thereby obtained are described in the present article. By the action of acrylonitrile on cyclohexanol, 2-methycyclohexanol and 3-methylcyclohexanol in the presence of a 40% aqueous solution of potassium hydroxide, the corresponding β-cyanethyl ethers (I), (II) and (III) were obtained in yields greater than 90%; during the hydrogenation of the latter with nickel catalyst in the presence of dry ammonia the γ-aminopropyl ethers (IV), (V) and (VI) were formed in yields of 95-96%:



$-OCH_2CH_2CN$
(I)
$-OCH_2CH_2CN$
CH_3
(II)
$-OCH_2CH_2CN$
CH_3
(III)
$-OCH_2CH_2CH_2NH_2$
(IV)
$-OCH_2CH_2CH_2NH_2$
(V)
CH_3
$-OCH_2CH_2CH_2NH_2$
CH_3
(VI)

The action of acrylonitrile on 1,2,5-trimethyl-4-piperidol (VII) leads to the formation of the β-cyanethyl ether (VIII) in almost quantitative yield (calculating on the basis of the piperidol which entered into the reaction). The latter (VIII) forms the γ-aminopropyl ether (IX) in a yield of 96% on hydrogenation with nickel catalyst in the presence of ammonia, and is converted in a yield of 80% to the β-carbethoxyethyl ether (X) by alcoholysis in the presence of sulfuric acid:



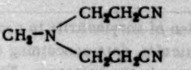
CH_3
CH_3-N
$-OCH_2CH_2CH_2NH_2$
CH_3
(IX)
$2H_2$, Ni
CH_3
CH_3-N
$-OH$
CH_3
(VII)
$CH_2{=}CHCN$
CH_3
CH_3-N
$-OCH_2CH_2CN$
CH_3
(VIII)
C_2H_5OH
H_2SO_4
CH_3
CH_3-N
$-OCH_2CH_2COOC_2H_5$.
(X)
CH_3

The alcoholysis of the cyanethyl ether (VIII) proceeds with considerable difficulty in comparison with ordinary nitriles and requires prolonged heating (18 hours) at a temperature not below 90°. We also conducted the addition of acrylonitrile to methylamine, dimethylamine and 2,5-dimethyl-4-piperidone with the object of studying the hydrogenation of the products thereby formed. Primary aliphatic amines, as is well known [1], add one molecule of acrylonitrile very readily, while the introduction of a secondmolecule requires extreme conditions (heating in a sealed ampoule) and in spite of all this still does not result in obtaining high yields of alkyl-di-(β-cyan ethyl)-amines.

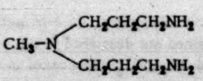
By heating acrylonitrile with methyl-β-cyanethylamine (XI) for 16 hours at 90° we obtained methyl-di(β-cyanethyl)-amine (XII) in a yield of 89%; by hydrogenating the latter in the presence of nickel catalyst and gaseous dry ammonia the methyldi-(γ-aminopropyl)-amine (XIII) was formed in a yield of 73%. 1-Methyl-1,5-diazacyclooctane (XIV), formed via cleavage of ammonia from the triamine (XIII) is also obtained at the same time as the product of a side reaction.

$CH_3NHCH_2CH_2CN$

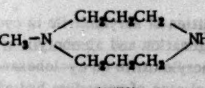
(XI)



(XII)



(XIII)



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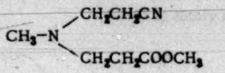
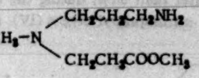
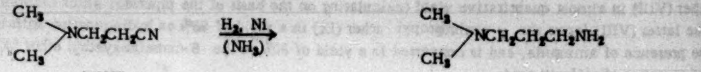


(XV)

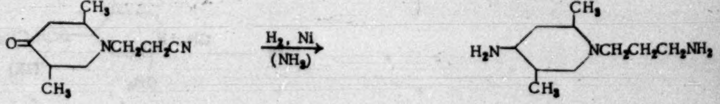


(XVI)

During the reaction of methyl-β-cyanethyl amine (XI) with methyl acrylate for 5 days at room temperature, methyl-β-cyanethyl-β-carbomethoxyethylamine (XV) was obtained in a yield of 92%; during the hydrogenation of the latter the amino-ether (XVI) should be formed. During the attempt to vacuum distil the hydrogenation product, however, it was converted into a polymerized mass and we did not succeed in isolating it in this manner. The β-cyanethyl derivatives (XVII) and (XVIII) obtained by the addition of acrylonitrile to dimethylamine and 2,5-dimethyl-4-piperidone, are converted by hydrogenation in the presence of nickel catalyst and dry gaseous ammonia into the corresponding γ-aminopropyl derivatives (XIX) and (XX) in a yield of about 80%.



(XVII) (XIX)



(XVIII) (XX)

Under these conditions, the hydrogenation of the nitrile group in compound (XVIII) is accompanied by reduction of the aminated carbonyl group.

EXPERIMENTAL

Addition of Acrylonitrile to Cyclohexanol. 105 g (1.98 mole) of acrylonitrile was added to a mixture of 193 g (1.93 mole) of cyclohexanol and 14 g of a 40% aqueous solution of potassium hydroxide while the mixture was being stirred vigorously. The temperature of the mixture was maintained below 30° by cooling with cold water and regulating the rate of addition of acrylonitrile. The stirring was continued at room temperature for 6 hours after the addition of the acrylonitrile and then the mixture was left overnight. The alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off, and the filtrate was vacuum distilled. 48 g of cyclohexanol was recovered and 208 g of the β-cyanethyl ether of cyclohexanol (I) was obtained:

b.p. 130-132° at 20 mm; n_D^{20} 1.4586; d_4^{20} 0.9674; MR_D 42.99; calc. 43.02.

10.139 mg sub.: 3.31 ml 0.02 N hyposulfite. 11.861 mg sub.: 3.57 ml 0.02 N hyposulfite. Found %: N 8.99, 8.74. $C_9H_{15}ON$. Calculated %: N 9.15.

The other experiments involving the addition of acrylonitrile were conducted analogously (see below).

Hydrogenation of the β-Cyanethyl Ether of Cyclohexanol. 35 g (0.23 mole) of the β-cyanethyl ether of cyclohexanol (I), 120 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 95-105° and the initial hydrogen pressure was 145 atm. The theoretical quantity of hydrogen (10.4 liter) was absorbed in 1 hour and 15 minutes. The product was filtered off from the catalyst and vacuum distilled. 34.5 g of the γ-aminopropyl ether of cyclohexanol (IV) was obtained:

b.p. 72-74° at 4.5 mm; n_D^{20} 1.4646; d_4^{20} 0.9281; MR_D 46.73; calc. 46.63 [2].

3.508 mg sub.: 0.284 ml N_2 (23°, 743 mm). 3.270 mg sub.: 0.266 ml N_2 (23°, 732 mm). Found %: N 9.13, 9.18. $C_9H_{19}ON$. Calculated %: N 8.92.

The phenylcarbamide with a m.p. of 101.5-102.5° (from benzene) was obtained.

Addition of Acrylonitrile to 2-Methylcyclohexanol. 142 g (1.24 mole) of 2-methylcyclohexanol, 10 g of a 40% aqueous solution of potassium hydroxide and 70 g (1.32 mole) of acrylonitrile were taken for the reaction. 42 g of the starting 2-methylcyclohexanol and 137.5 g of the β-cyanethyl ether of 2-methylcyclohexanol (II) were obtained:

b.p. 134-137° at 18 mm; n_D^{20} 1.4564; d_4^{20} 0.9502; MR_D 47.81; calc. 47.64.

9.270 mg sub.: 2.20 ml 0.02 N hyposulfite. 5.750 mg sub.: 1.76 ml 0.02 N hyposulfite. Found %: N 8.18, 8.31. $C_{10}H_{17}ON$. Calculated %: N 8.38.

Hydrogenation of the β-Cyanethyl Ether of 2-Methylcyclohexanol. 34.5 g (0.2 mole) of the β-cyanethyl ether of 2-methylcyclohexanol (II), 130 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 150 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed in 1 hour 20 minutes. The reaction mass was cooled, the nickel filtered off and the filtrate vacuum distilled. After distilling off the methanol 34 g of the γ-aminopropyl ether of 2-methylcyclohexanol (V) was obtained:

b.p. 73-74.5° at 3.5 mm; n_D^{20} 1.4603; d_4^{20} 0.9115; MR_D 51.39; calc. 51.24.

7.537 mg sub.: 0.554 ml N_2 (22°, 754 mm). 3.581 mg sub.: 0.264 ml N_2 (22°, 750 mm). Found %: N 8.34, 8.42. $C_{10}H_{21}ON$. Calculated %: N 8.18.

The phenylcarbamide with a m.p. of 96-98° was prepared.

Reaction of 3-Methylcyclohexanol with Acrylonitrile. 114 g (1 mole) of 3-methylcyclohexanol, 7 g of a 40% aqueous solution of potassium hydroxide and 53 g (1 mole) of acrylonitrile were taken. 37.5 g of the starting 3-methylcyclohexanol and 109.5 of the β-cyanethyl ether of 3-methylcyclohexanol (III) were obtained:

b.p. 133-136° at 16 mm; n_D^{20} 1.4529; d_4^{20} 0.9458; MR_D 47.82; calc. 47.64.

7.975 mg sub.: 2.38 ml 0.02 N hyposulfite. 7.370 mg sub.: 2.25 ml 0.02 N hyposulfite. Found %: N 8.44, 8.63. $C_{10}H_{17}ON$. Calculated %: N 8.38.

Hydrogenation of the β-Cyanethyl Ether of 3-Methylcyclohexanol. 27.6 g (0.16 mole) of the β-cyanethyl ether of 3-methylcyclohexanol (III), 120 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (7.2 liters) was absorbed in 45 minutes. 26.9 g of the γ-aminopropyl ether of 3-methylcyclohexanol (VI) was obtained:

b.p. 76-78° at 4 mm; n_D^{20} 1.4599; d_4^{20} 0.9118; MR_D 51.35; calc. 51.24.

5.245 mg sub.: 0.392 ml N_2 (22°, 748 mm). 3.640 mg sub.: 0.274 ml N_2 (21°, 749 mm). Found %: N 8.53, 8.39. $C_{10}H_{21}ON$. Calculated %: N 8.18.

Reaction of Acrylonitrile with 1,2,5-Trimethyl-4-piperidol. 17 g (0.32 mole) of acrylonitrile was added to a vigorously stirred mixture of 45 g (0.314 mole) of 1,2,5-trimethyl-4-piperidol (VII) and 3 g of a 40% aqueous solution of potassium hydroxide. The temperature spontaneously rose to 35° and fell to 21° after an hour. The stirring was continued at room temperature for 4 hours after this, and the mixture was then left overnight. The alkali was neutralized with an equivalent quantity of hydrochloric acid, the potassium chloride which settled out was filtered off, and the filtrate vacuum distilled. 14.1 g of the starting piperidol (VII) and 42 g of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII) in the form of a colorless oil with a characteristic amine odor was obtained:

b.p. 117° at 4 mm; n_D^{20} 1.4635; d_4^{20} 0.9661; MR_D 55.97; calc. 56.20.

9.940 mg sub.: 5.07 ml 0.02 N hyposulfite. 11.059 mg sub.: 5.67 ml 0.02 N hyposulfite. Found %: N 14.25, 14.50. $C_{11}H_{18}ON_2$. Calculated %: N 14.28.

The picrate with a m.p. of 111-113° (from a mixture of alcohol and acetone) was obtained.

Hydrogenation of the β-Cyanethyl Ether of 1,2,5-Trimethyl-4-piperidol. 19.6 g (0.1 mole) of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII), 100 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 125 atm. The theoretical quantity of hydrogen (4.5 liters) was absorbed in 35 minutes. 19.2 g of the γ-aminopropyl ether of 1,2,5-trimethyl-4-piperidol (IX) was obtained:

b.p. 116-118° at 8 mm; n_D^{20} 1.4680; d_4^{20} 0.9315; MR_D 59.80; calc. 59.68.

21.383 mg sub.: 6.50 ml 0.02 N hyposulfite. 17.038 mg sub.: 9.53 ml 0.02 N hyposulfite. Found %: N 14.05, 13.90. $C_{11}H_{24}ON_2$. Calculated %: N 14.00.

The picrate with a m.p. of 147-149° (from alcohol) was obtained.

Alcoholysis of the β-Cyanethyl Ether of 1,2,5-Trimethyl-4-piperidol. a) A mixture of 20 g (0.1 mole) of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII), 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred for 18 hours at 90° (the mixture boiled at this temperature). After cooling, 100 ml of water was poured in; the product was neutralized with soda, salted out with potash, extracted with ether, dried with sodium sulfate and vacuum distilled. 20.2 g of the β-carbethoxyethyl ether of 1,2,5-trimethyl-4-piperidol (X) was obtained:

b.p. 109-110° at 4 mm; n_D^{20} 1.4504; d_4^{20} 0.9807; MR_D 66.64; calc. 67.27.

4.955 mg sub.: 0.239 ml N_2 (20°, 751 mm). 4.680 mg sub.: 0.235 ml N_2 (20°, 751 mm). Found %: N 5.53, 5.78. $C_{13}H_{25}O_3N$. Calculated %: N 5.76.

The hydrochloride with a m.p. of 93.5-95° was obtained.

b) Alcoholysis did not occur when a mixture of 40 g of the β-cyanethyl ether (VIII), 100 ml of methyl alcohol and 50 g of concentrated sulfuric acid was heated for 8 hours at 70°, and the β-cyanethyl ether (VIII) was recovered in a quantity of 24 g.

Reaction of Acrylonitrile with Methylamine. To a mixture of 122 g (4 moles) of methylamine in 700 ml methanol which was vigorously stirred and cooled with ice water, 208 g (4 moles) of acrylonitrile was added over a period of 2 hours at such a rate the temperature of the mixture did not rise above 30°. The stirring was continued at room temperature for 10 hours after addition of the acrylonitrile. After distilling off the methyl alcohol and vacuum distilling the product, 255.5 g of the β-cyanethylmethylamine (XI) was obtained:

b.p. 86° at 25 mm; n_D^{20} 1.4320 [3].

In addition, 54 g of di-(β-cyanethyl)-methylamine (XII) was obtained:

b.p. 162-164° at 6 mm; n_D^{20} 1.4606.

Reaction of Acrylonitrile with β-Cyanethylmethylamine. A mixture of 21.5 g (0.25 mole) of β-cyanethylmethylamine (XI) and 16 g (0.3 mole) of acrylonitrile was heated with a reflux condenser at 90° for 16 hours. 31.2 g of di-(β-cyanethyl)-methylamine (XII) was obtained:

b.p. 159.5-160° at 5 mm; n_D^{20} 1.4612 [3].

Hydrogenation of Di-(β-cyanethyl)-methylamine. 13.7 g (0.1 mole) of di-(β-cyanethyl)methylamine (XII), 60 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (9 liters) was absorbed in 1.5 hours. 10.6 of di-(γ-aminopropyl)-methylamine (XIII) was obtained:

b.p. 81-83° at 4 mm; n_D^{20} 1.4753; d_4^{20} 0.9023; MR_D 45.26; calc. 45.31.

6.183 mg sub.: 1.558 ml N_2 (20°, 754 mm). 4.556 mg sub.: 1.164 ml N_2 (22°, 753 mm). Found %: N 29.13, 29.29. $C_7H_{19}N_3$. Calculated %: N 28.97.

1-Methyl-1,5-diazacyclooctane (XIV) in the form of the hydrochloride with a m.p. of 189.5-190° (from alcohol) was isolated from the low boiling fraction.

2.585 mg sub.: 0.3862 ml N_2 (20°, 736 mm). 2.345 mg sub.: 0.3519 ml N_2 (20°, 744 mm). Found %: N 16.84, 17.13. $C_7H_{17}N_2Cl$. Calculated %: N 17.02.

Reaction of β-Cyanethylmethylamine with Methyl Acrylate. 21.5 g (0.25 mole) of the methyl ether of acrylic acid was added in small portions to 21 g (0.25 mole) of β-cyanethylmethylamine (XI) which was being stirred and cooled with ice water. The temperature of the mixture did not rise above 30°. After the spontaneous evolution of heat had ceased, the flask was closed and left at room temperature for 5 days. 39.3 g of β-carbomethoxyethyl-β-cyanethylmethylamine (XV) was obtained:

b.p. 133° at 6 mm; 114° at 4.5 mm; n_D^{20} 1.4507; d_4^{20} 1.0338; MR_D 44.25; calc. 44.56.

7.216 mg sub.: 1.020 ml N_2 (21°, 756 mm). 8.725 mg sub.: 1.254 ml N_2 (21°, 756 mm). Found %: N 16.70, 16.60. $C_8H_{14}O_2N_2$. Calculated %: N 16.47.

The picrate was obtained with a m.p. of 108-109° (from alcohol).

Hydrogenation of β-Carbomethoxyethyl-β-cyanethylmethylamine. 34 g (0.2 mole) of the nitrile ether (XV), 50 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were placed in a 152 ml rotary autoclave. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (9 liters) was absorbed after 1.5 hours. The mixture was cooled, the nickel filtered off and the methyl alcohol eliminated in a vacuum on a water bath, the temperature of which did not rise about 50°. Under these conditions the liquid in the flask acquired a more and more viscous consistency and finally was converted into a rubber-like, dark brown, polymerized mass.

Reaction of Acrylonitrile with Dimethylamine. 318 g (6 moles) of acrylonitrile was added to a solution of 270 g (6 moles) of di methylamine in 400 g of methyl alcohol which was being stirred vigorously and cooled with ice water, at such a rate that the temperature of the mixture did not exceed 30°. After cessation of the spontaneous evolution of heat the mixture was stirred at 40-55° for 1 hour and then left overnight. After distilling off the methyl alcohol and vacuum distilling the product, 566.5 g of β-dimethylaminopropionitrile (XVII) was obtained:

b.p. 60-61° at 10 mm, 68° at 18 mm; n_D^{20} 1.4282 [4, 5].

Hydrogenation of β-Dimethylaminopropionitrile. 200 g (2 mole) of β-dimethylaminopropionitrile (XVII), 1220 ml of methyl alcohol, saturated with dry ammonia and 10 g of Raney nickel were taken. The hydrogenation was conducted at 80-90° and the initial hydrogen pressure was 85 atm. The theoretical quantity of hydrogen was absorbed in 45 minutes. 134 g of γ-dimethylaminopropylamine (XIX) with a b.p. of 131-134° at 758 mm; n_D^{20} 1.4398, was obtained by repeated fractional distillation.

57 g of the hydrochloride of γ-dimethylaminopropylamine with a m.p. of 183-184° (from methyl alcohol) [4, 5] was isolated in addition by saturating the methyl alcohol driven off and the low boiling fractions with dry hydrogen chloride.

Reaction of Acrylonitrile with 2,5-Dimethyl-4-piperidone. A mixture of 127 g (1 mole) of 2,5-dimethyl-4-piperidone and 53 g (1 mole) of acrylonitrile was heated at 95-97° for 3 hours and then left overnight at room temperature. 104 g of the starting piperidone and 31.2 g of 1-(β-cyanethyl)-2,5-dimethyl-4-piperidone (XVIII) in the form of a colorless viscous oil were obtained:

b.p. 143-145° at 5.5 mm; n_D^{20} 1.4841; d_4^{20} 1.0345; MR_D 49.79; calc. 49.95.

2.055 mg sub.: 0.278 ml N_2 (21°, 740 mm). 2.870 mg sub.: 0.394 ml N_2 (21°, 740 mm). Found %: N 15.30, 15.50. $C_{10}H_{16}ON_2$. Calculated %: N 15.55.

Hydrochloride m.p. 166.5-167° (from acetone).

Picrate m.p. 136-137° (from acetone).

Hydrogenation of 1-(β-Cyanethyl)-2,5-dimethyl-4-piperidone. 13.3 g (0.075 mole) of 1-(β-cyanethyl)-2,5-dimethyl-4-piperidone (XVIII), 100 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 100-110° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (5 liters) was absorbed in one hour. 10.6 g of 1-(γ-aminopropyl)-2,5-dimethyl-4-amino piperidine (XX) was obtained:

b.p. 108-110° at 3.5 mm; n_D^{20} 1.4917; d_4^{20} 0.9475; MR_D 56.72; calc. 56.96.

4.535 mg sub.: 0.896 ml N_2 (20°, 751 mm). 4.595 mg sub.: 0.892 ml N_2 (20°, 754 mm). Found %: N 22.79, 22.49. $C_{10}H_{23}N_3$. Calculated %: N 22.70.

The picrate with a m.p. of 227.5-228.5° (from a mixture of alcohol and acetone) was obtained.

SUMMARY

1. By the addition of acrylonitrile to cyclohexanol, 2- and 3-methylcyclohexanols, and also to 1,2,5-trimethyl-4-piperidol, the corresponding β-cyanethyl ethers (I), (II), (III) and (VIII) were obtained in yields greater than 90%; by the hydrogenation of the latter under pressure in the presence of nickel catalyst and dry gaseous ammonia the γ-aminopropyl ethers (IV), (V), (VI), and (IX) were obtained in yields of 95%.

2. The carbethoxyethylether of piperidol (X) was also obtained during the alcoholysis of the β-cyanethyl ether (VIII).

3. The addition of methyl-β-cyanethylamine (XI) to acrylonitrile and methyl acrylate was accomplished and compounds (XII) and (XV) were thus obtained in high yields.

4. The hydrogenation of the β-cyanethyl derivatives (XII), (XVII), and (XVIII) in the presence of ammonia was described and the corresponding γ-aminopropyl derivatives (XIII), (XIX) and (XX) were obtained in high yields.

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PYRIDINE DYE DERIVATIVES OF DIPHENYL

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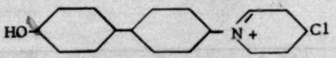
Pyridine dye derivatives of diphenyl have hardly been studied at all. We obtained and investigated four symmetrical dyes (I), (II), (III), (IV) and the quaternary pyridine salts corresponding to them (see table) by the reaction of the 2,4-dinitrochlorophenylate of pyridine with benzidine, 4-aminodiphenyl, 4-nitro-4'-aminodiphenyl and the p-aminochlorodiphenylate of pyridine.

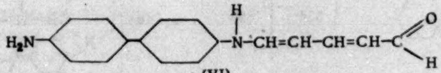
The dyes obtained, in contrast to the phenyl derivatives investigated by us [1], were decomposed with difficulty in solutions. On heating the dry substance to a determined temperature the original color disappears; the dye is decomposed in the course of 15-30 minutes without melting. Only the derivatives of the p-aminochlorodiphenylate of pyridine (II) and 4-nitro-4'-aminodiphenyl (IV) decomposed according to the usual pattern [2] for an amine and the corresponding quaternary pyridine salt. Independent compounds were formed from the derivatives of benzidine and 4-aminodiphenyl, the composition of which agrees with that of the starting dye.

The yellow substance obtained after heating the benzidine derivative (VI) in the dry form at 180° was investigated in detail. The finely crystalline powder with a m.p. of 273° when recrystallized from water crystallized with the solvent. It crystallized from methyl alcohol in the form of shiny yellow plates with a m.p. of 277°. The substance began to sublime during heating to 280-200° and the sublimation continued even after fusion; the sublimed substance had a bright orange color and did not contain solvent, but rapdily yellowed in the air and attracted moisture; it did not melt on heating to 300°. The presence of three amine groups was determined by diazotization. After boiling the diazo solution two substances were isolated – the p-hydroxychlorodiphenylate of pyridine (V) and 4,4-dihydroxydiphenyl (with a m.p. of 270°).



(V)

The yellow substance did not react with alkali in the cold and it was only after boiling it with an alkaline solution that a red substance – the product of the cleavage of the p-aminochlorodiphenylate of pyridine (VI) and benzidine was isolated.



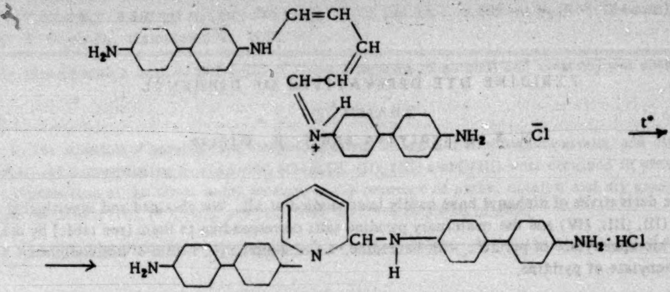
(VI)

The capacity to sublime and the behavior toward alkali are evidence of the considerable stability of the substance.

The substance condenses with the 2,4-dinitrochlorophenylate of pyridine and two dyes are thereby formed – the derivatives of the p-aminochlorodiphenylate of pyridine and benzidine, but the reaction proceeds slowly and the dyes are obtained in low yield.

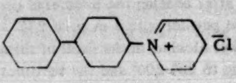
Although the diazotization determined three amine groups, on the basis of which it could be assumed that the yellow substance consisted of a molecular compound of the quaternary pyridine salt – the p-aminochlorodiphenylate of pyridine and benzidine, the great stability of the substance and also the absence of molecular compounds in the thermal decomposition products of the two other dyes (II), and (IV), raise doubts concerning the correctness of such an assumption.

It is highly probable that isomerization of the molecule without elimination of an amine proceeds during the heating of the dye:



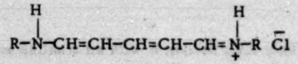
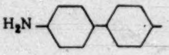
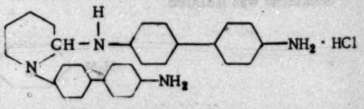
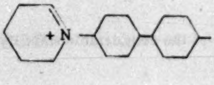
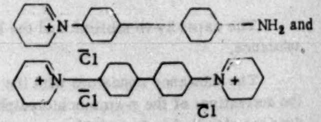
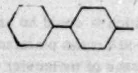
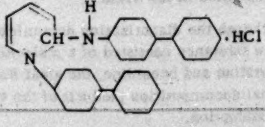
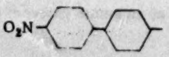
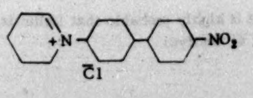
The substance formed — the hydrochloride of (N-p-aminodiphenyl-α-hydro-4,4'-diaminodiphenyl)-pyridine — is decomposed during diazotization into the p-aminochlorodiphenylate of pyridine and benzidine which are then diazotized.

The yellow substance obtained by heating the diphenyl derivative (III) is less stable, in contrast to the benzidine derivative. It decomposes during recrystallization from water into the chlorodiphenylate (VII) and 4-aminodiphenyl.



(VII)

The diverse behavior of the diphenyl derivatives during heating, as well as their color, is associated with the character of the amine radicals — the greater the basicity of the amine, the more stable the dye corresponding to it and the deeper its color (see the table).

Significance of R in the dye formula  $R-\overset{H}{N}-CH=CH-CH=CH-CH=\underset{+}{\overset{H}{N}}-R\ \bar{C}l$		λmax. (in mμ)		Decomposition temperature (in °C)	Salts obtained by the termal decomposition of the dye
		in ethyl alcohol	in ethyl alcohol and HCl		
(I)		535	526	180	
(II)		510	510	230	
(III)		516	522	150	
(IV)		*	530	135	

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* The dye hydrolyzes in neutral solution.

EXPERIMENTAL

Chloride of 1,5-Bis-(4,4'-aminodiphenyl)-pentadiene-1,3-ylidiene-5

An alcoholic solution of benzidine (5.2 g in 15 ml) was poured into a solution of 4 g of the 2,4-dinitrochlorophenylate of pyridine in 10 ml of ethyl alcohol; a rich cherry-red coloration at once appeared and the mixture crystallized. After the solution had been heated for 5 minutes on a boiling water bath and had been cooled, the dye was filtered off, washed several times with warm acetone to free it from the dinitroaniline, with hot water to free itfrom the quaternary salt, and with a small quantity of alcohol and ether. 6 g (89%) of the thus purified dye was obtained. It consisted of completely homogeneous crystals under the microscope. 2 g of the dye was heated with 150 ml of ethyl alcohol, but most of it (1.7 g) did not dissolve. After the solution had stood for a day, 0.01 g of dye in the form of a finely crystalline green powder that did not melt on heating to 300° was obtained. It contained chlorine. It crystallized with the solvent; this was difficult to determine quantitatively, since the dye became hygroscopic after elimination of the solvent.

Found %: N 10.72, 10.68. $C_{29}H_{27}N_4Cl \cdot 1\,1/4C_2H_5OH$. Calculated %: N 10.69.

Decomposition of the Dye. 1 g of the dye in 150 ml of alcohol was heated for 8 hours with 3 ml of hydrochloric acid (d 1.19) on a boiling water bath. The dye which did not decompose (0.45 g) was filtered off, the alcohol distilled off and the brown precipitate which remained was recrystallized from water. 0.4 g of a yellow substance, soluble in hot water and poorly soluble in alcohol was obtained; the substance did not dissolve in ether, contained chlorine, and crystallized with the solvent, m.p. 273°. Benzidine was not detected. The content of nitrogen in the yellow substance was higher than in the p-aminochlorodiphenylate of pyridine, which should be formed during the decomposition of the dye according to the usual pattern.

Found %: N 10.56, 10.57. $C_{17}H_{15}N_2Cl \cdot H_2O$. Calculated %: N 9.31. $C_{29}H_{27}N_4Cl \cdot 4H_2O$. Calculated %: N 10.40

The dye was more readily decomposed in water in the presence of hydrochloric acid, but still slowly. It was noted during the attempt to determine the melting point of the dye that the dye became brown at 160-180° and did not change on heating to 270°. 2.2 g of a light-brown substance was obtained after heating 2.3 g of the dye at 170-180° for 15-20 minutes in a desiccator. A yellow, finely crystalline powder with m.p. 273° was obtained after crystallization from 250 ml of water. The melting point of a mixed sample with the substance obtained after decomposition of the dye in alcohol was not depressed. It crystallized from methyl alcohol in the form of shiny yellow needles, m.p. 277°. It contained solvent. 1 g of the substance was sublimed in a covered glass crucible. The bright-yellow sublimate, which did not melt on heating to 300°, rapidly attracted moisture on exposure to air and became yellow.

Found %: N 11.69, 11.70; Cl 7.11, 7.38. Calculated %: N 11.56; Cl 7.33.

1 g of the substance consumed 10.4 ml of 0.5 N $NaNO_2$ (with a $K_{\text{instability}} = 1.1$) on diazotization, which corresponded to the presence of three amine groups. The diazo solution was heated until the evolution of nitrogen bubbles ceased. After cooling, an orange precipitate settled out which recrystallized from water in the form of a finely crystalline powder, slightly tinged with a rose color (0.6 g); it consisted of heterogeneous crystals under the microscope. The substance was treated with ether several times and was twice recrystallized from aqueous alcohol (4:1). 0.2 g of material, which consisted of colorless needles under the microscope, was obtained. It did not melt on heating to 300° and contained solvent.

Found %: N 4.29, 4.15. $C_{17}H_{14}NOCl \cdot 3H_2O$. Calculated %: N 4.15.

A colorless substance was isolated from the ethereal solution which agreed in its melting point (270°) with that of 4,4'-dihydroxydiphenyl.

1 g of the yellow substance, dissolved by heating in 100 ml of water, was poured into a hot solution of 5 ml of 25% sodium hydroxide. A red color at once appeared and a brownish-red precipitate settled out. The mixture was boiled for a half hour and filtered while hot. 0.5 g of a brownish-red precipitate was obtained which was carefully washed with water until the alkali was eliminated. The precipitate was heated with 200 ml of acetone and 0.3 g dissolved. After a day an insignificant quantity of a brown substance that did not contain chlorine precipitated. An intense red color appeared during the addition to an acetone or alcohol solution of drops of hydrochloric acid. A solution of the substance in acetic acid was violet colored (unstable). The substance contained solvent. Its properties agreed with those of the alkaline cleavage product of a quaternary pyridine salt.

Found %: N 8.81, 8.77. $C_{17}H_{16}N_2O \cdot CH_3COCH_3$. Calculated %: N 8.69.

After concentration and decolorizing the aqueous filtrate, benzidene was isolated.

Condensation of the Yellow Substance with the 2,4-Dinitrochlorophenylate of Pyridine. A solution of 3.5 g of the dinitrochlorophenylate of pyridine in 15 ml of methyl alcohol was added to a solution of 5 g of the yellow substance in 190 ml of methyl alcohol. During the mixing of the hot solutions a weak red color appeared. In 4-5 minutes after beginning the heating of the mixture, green crystals settled on the walls of the flask. Heating was continued for 20 minutes on a boiling water bath. The precipitate which formed was washed on the filter with ether, hot water, acetone and again with ether. 2.43 g of a mixture of dyes was obtained. In view of the poor solubility of the dyes in organic solvents, attempts to separate them by crystallization were unsuccessful. We succeeded in separating the dyes only by decomposing one of them during prolonged boiling of the mixture in acidified water. The undecomposed preparation was separated by centrifuging, and washed with water, acetone and ether. The dye contained solvent.

Found %: N 7.78, 7.75. $C_{39}H_{33}N_4Cl_3 \cdot 2CH_3OH$. Calculated %: N 7.70.

Thermal Decomposition of the Chloride of 1,5-Bis-(4-aminochlorodiphenylate)-pentadiene-1,3-ylidene-5. 0.4 g of the dye (which did not decompose when the mixture was boiled in water) was heated in a desiccator at 230° for 30 minutes. A precipitate that was completely insoluble in water was probably a residue (0.1 g) of carbonized dye. The solution was completely boiled down on a water bath and the brown substance which remained was dissolved in alcohol from which it did not settle out and from which it was, consequently, precipitated with acetone. The precipitate operation was repeated twice. 0.06 g of light yellow substance was obtained, which was quite soluble in water and did not melt on heating to 300°.

Found %: N 7.03, 7.09; Cl 15.97. $C_{22}H_{18}N_2Cl_2 \cdot C_2H_5OH$. Calculated %: N 6.56; Cl 16.63.

The high analytical results for nitrogen and the low results for chlorine can be explained by admixture of the p-aminochlorodiphenylate of pyridine which is formed along with the dipyridine salt, but which we could not isolate.

Chloride of 1,5-Bis-(4-aminodiphenyl)-pentadiene-1,3-ylidene-5

A mixture of 2 g of the 2,4-dinitrochlorophenylate of pyridine and 1.94 g of 4-aminodiphenyl [3] in 20 ml of ethyl alcohol was heated for 10 minutes on a water bath. After cooling, the mixture was mixed with ether, the precipitate was washed on the filter with ether and water and recrystallized from ethyl alcohol. 1.5 g (56.8%) of the dye was obtained in the form of fine, silky, red crystals with a bluish-green sheen. They consisted of violet plates under the microscope. M.p. 151-152°. The crystals contained solvent.

Found %: N 6.15, 6.17. $C_{29}H_{25}N_2Cl \cdot 1/2C_2H_5OH$. Calculated %: N 6.09.

Thermal Decomposition of the Dye. 0.6 g of the dye was heated in a desiccator for 1 hour at 150°. 0.57 g of an orange product was obtained which was recrystallized from water. Upon dissolving it in hot water the separation of a brown oil was observed which proved to be 4-aminodiphenyl. 0.4 g of a yellow flaky substance was obtained from the aqueous solution, which darkened on heating above 150°, was quite soluble in alcohol, water and acetone; and was insoluble in ether. It contained solvent. A test for chlorine was positive. It did not react with alkali without heating. The substance was almost completely decomposed by repeated crystallization from water into 4-aminodiphenyl and the chlorodiphenylate of pyridine. A small residue was recrystallized from ethyl alcohol in the presence of carbon and washed well with ether.

Found %: N 5.93, 5.89. $C_{29}H_{25}N_2Cl \cdot C_2H_5OH$. Calculated %: N 5.80.

The aqueous solution after separation of the yellow substance was decolorized with carbon and concentrated to 2-3 ml. Coarse needle-shaped colorless crystals (0.12 g) settled out after several hours. The substance contained chlorine, crystallized with the solvent, and melted at 110-112°.

Found %: N 5.01. $C_{17}H_{14}NCl \cdot H_2O$. Calculated %: N 4.90.

Repeated purification of the substance was conducted by reprecipitating it from alcohol with ether. A finely crystalline product was obtained which contained solvent and melted at 112°.

Found %: N 4.48. $C_{17}H_{14}NCl \cdot C_2H_5OH$. Calculated %: N 4.46.

The chlorodiphenylate of pyridine was quite soluble in water and alcohol and less soluble in acetone. A red color appeared and a brown precipitate settled out during the addition of alkali to an aqueous solution. After recrystallization from acetone, a red powder which contained solvent was obtained.

Found %: N 5.22, 5.16. $C_{17}H_{15}NO \cdot 1/2CH_3COCH_3$. Calculated %: N 5.03.

Chloride of 1,5-Bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,3-ylidene-5

A mixture of 3 g of 4-nitro-4'-aminodiphenyl and 2.7 g of the 2,4-dinitrochlorophenylate of pyridine in 50 ml of ethyl alcohol was heated on a boiling water bath for 50 minutes. 1.6 g (39.9%) of the dye was obtained and washed with acetone and water. 0.2 g of the dye was recrystallized from 50 ml of ethyl alcohol. 0.1 g of fine green crystals with a metallic sheen was obtained. The dye was readily precipitated from alcoholic solution by mild acidification with hydrochloric acid. During prolonged heating of the alcoholic solution or during considerable dilution with alcohol the orange-red color disappeared and the solution became yellow. The dye was soluble in acetic acid and crystallized very well from it.

With the object of increasing the yield of dye the condensation of the starting materials was conducted in the presence of pyridine; 1 g of amine was dissolved by heating in 7 ml of pyridine, and a hot solution of 1 g of the initial salt in 10 ml of ethyl alcohol was poured into this solution. A red color at once appeared and in 2-3 minutes after the beginning of the heating the mixture crystallized. On the following day the mixture was diluted with acetone, and the precipitate on the filter was washed with warm acetone, hot water, ether, and again with acetone. 1.25 g (93.5%) of a dark-green, finely crystalline dye was obtained. A portion of it was recrystallized from alcohol. It crystallized with the solvent.

Found %: N 9.84, 9.89. $C_{29}H_{23}N_4O_4Cl \cdot C_2H_5OH$. Calculated %: N 9.78.

Decomposition of the Dye. After heating 1 g of the dye for an hour at 135° the initial color disappeared and a mixture of orange and brown crystals was formed. After treating the mixture with hot water 0.55 g of 4-nitro-4'-aminodiphenyl (m.p. 200°) was obtained. A quaternary salt – the chloride of the p-nitrodiphenylate of pyridine – was obtained in the form of fine light-yellow needles from the mother liquor after separation of the amine, decolorizing the solution with carbon and concentrating it. The material contained chlorine. A test for presence of solvent was positive.

Found %: N 7.85, 7.78. $C_{17}H_{13}N_2O_2Cl \cdot C_2H_5OH$. Calculated %: N 7.81.

The quaternary salt was readily soluble in water, and was cleaved by alkali in the cold with the formation of a red substance.

SUMMARY

1. The following three pyridine dyes which had not been described previously were synthesized: the chloride of 1,5-bis-(4-aminodiphenyl)-pentadiene-1,3-ylidene-5, the chloride of 1,5-bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,3-ylidene,5, and the chloride of 1,5-bis-(p-aminochlorodiphenylate of pyridine)-pentadiene-1,3-ylidene-5.

2. A hypothesis was proposed to the effect that during the heating of the dye derivatives of benzidine and of 4-aminodiphenyl, isomeric transformation of the molecule without amine cleavage occurs.

3. The following four quaternary pyridine salts which had not been described previously were prepared: 4,4'-bis-(pyridine chloride)-N,N'-diphenyl, the chlorodiphenylate of pyridine, the 4-nitrochlorodiphenylate of pyridine, and the 4-hydroxychlorodiphenylate of pyridine.

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Chloride of 1,5-bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,5-ylidene-4 [illegible]

A mixture of 2 g of [illegible] and [illegible] g of 4-nitro-4'-aminodiphenyl [illegible] of ethyl alcohol was [illegible] on a boiling water bath [illegible]. [illegible] g of the dye [illegible] and washed with acetone and water; 0.7 g of the dye was recrystallized from [illegible] of ethyl alcohol; [illegible] g of fine [illegible] crystals with a [illegible] luster was obtained. The dye was [illegible] with hydrochloric acid. During [illegible] heating [illegible] the unchanged [illegible] was [illegible] and the [illegible]. The dye was soluble in [illegible] acid and crystallized very well from it.

With the object of increasing the yield of dye the condensation of the starting materials was conducted in the presence of pyridine: 1 g of amine was dissolved by heating in 5 ml of pyridine, and a hot solution of [illegible] g of the [illegible] salt in 15 ml of ethyl alcohol was poured into this solution. A red color at once appeared and [illegible] after the beginning of the heating the mixture was filtered. On the following day the mixture was diluted with acetone, and the precipitate on the filter was washed with warm acetone, hot water, ether, and again with acetone. [illegible] g ([illegible] %) of a dark green, finely crystalline dye was obtained. A sample of it was recrystallized from alcohol. It crystallized with [illegible].

Found %: N 8.84, 8.88. [illegible]. Calculated %: N [illegible].

Decomposition of the dye. After heating [illegible] g of the dye for an hour at 100° the initial color [illegible] and a mixture of orange and brown crystals was formed. After treating the mixture with hot water [illegible] g of [illegible] amine, m.p. 200°, was obtained. A quaternary salt – the chloride of the [illegible] of pyridine – was obtained in the form of fine light-yellow needles from the mother liquor after separation of the amine, [illegible] the solution with [illegible]. The substance contained chlorine. A test for [illegible] was positive.

Found %: N [illegible]. [illegible]. Calculated %: N [illegible].

The quaternary salt was readily soluble in water, and was [illegible] by alkali, in the cold with the formation of a red solution.

SUMMARY

1. The following three pyridine dyes which had not been described previously were synthesized: the chloride of 1,5-bis-(4-aminodiphenyl)-pentadiene-1,5-ylidene-4, the chloride of 1,5-bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,5-ylidene-4, and the chloride of 1,5-bis-[illegible] pentadiene-1,5-ylidene-4.

2. A hypothesis was proposed to the effect that during the heating of the dye derivatives of benzidine and of aminodiphenyl a [illegible] transformation of the [illegible] occurs.

3. The following four quaternary pyridine salts which had not been described previously were prepared: [illegible] of pyridine, the chloride [illegible] of pyridine, the [illegible] of pyridine, and the [illegible] of pyridine.

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INVESTIGATION OF ORGANIC ISOCYNATES

III. REACTION OF AROMATIC ISOCYANATES WITH HALOGENS

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As early as 1887 Gumpert [1] described the labile addition products formed by the action of chlorine or bromine on a solution of phenylisocyanate in chloroform.

According to Gumpert, these substances are readily decomposed into their components and evolve iodine from a solution of iodide salts; the bromine addition product is converted by heating into 4-bromophenylisocyanate with evolution of hydrogen bromide. These data were confirmed by Curtius [2, 3] in 1895 and 1913 as relates to the bromine addition product. Curtius also carried out another method of preparation – the reaction of benzazide with bromine in chloroform and gave a more precise description of the properties of the substance: m.p. 144°, it sublimates without decomposition during careful heating, and is smoothly converted into 4-bromophenylisocyanate with evolution of HBr only when its vapors are superheated.

Siefken confirmed in a recently published work [4] on the basis of experiments involving the chlorination of phenylisocyanate in tetrachloroethane that Gumpert had not clarified the nature of the reaction products of chlorine and phenylisocyanate. Actually, the acid chloride of phenylcarbamic acid is initially formed and later on compounds containing chlorine in the benzene ring.

In our experiments involving the reaction of chlorine and bromine with phenyl, 4-tolyl-, 4-nitrophenyl- and 1-naphthylisocyanate we did not succeed in observing the addition products described by Gumpert and Curtius. A colorless crystalline compound is evolved by the action of chlorine and bromine on a solution of phenylisocyanate in chloroform, which, according to the analysis, contains 2 atoms of halogen per isocyanate molecule. The compounds obtained yield a weak coloration with a solution of potassium iodide and starch which disappears as a result of the addition of 1-2 drops of 0.1 N thiosulfate. One equivalent of acid was detected by titration with alkali. When the substance is heated, it is converted into halogen-substituted phenylisocyanates; with alcohol it yields esters of halogenphenylcarbamic acid and with concentrated sulfuric acid 4-chloro- and 4-bromoanilines. A substance identical with that obtained by the action of bromine on phenylisocyanate and agreeing in properties with that described by Curtius, was formed by the addition of the elements of hydrogen bromide to 4-bromophenylisocyanate and, consequently, actually consists of the acid bromide of 4-bromophenylcarbamic acid.

It is of interest that the phenyl-, 4-tolyl- and 4-nitrophenylisocyanates did not yield reaction products with equimolecular quantities of chlorine in carbon tetrachloride.

If a small quantity of dry hydrogen chloride is introduced into a solution of phenylisocyanate and chlorine in carbon tetrachloride, then a precipitate of the acid chloride of 4-chlorophenylcarbamic acid settles out. In contrast to the isocyanates of the benzene series, 1-naphthylisocyanate in carbon tetrachloride forms the acid chloride of 4-chloro-1-naphthylcarbamic acid directly by the action of chlorine. The difference in the behavior of phenyl- and 1-naphthylisocyanates is also observed during their reaction with sulfuryl chloride. Phenylisocyanate does not react appreciably and a mixture of the substances can be separated by fractional distillation at normal pressure; 1-naphthylisocyanate yields the acid chloride of 4-chloro-1-naphthylcarbamic acid even while being cooled.

Thus, in agreement with Siefken, the reaction of halogens with arylisocyanates at low temperatures ought to be considered as a halogenation of arylcarbamic acid derivatives. The substituent initially enters in the para-position which is usually also observed in other cases of halogenation of acylaminoderivatives. The presence in the reaction mass of hydrogen halide is necessary to initiate the reaction. The latter, evidently, can be formed either as a result of reaction with the solvent (chlorination and bromination of phenylisocyanate in chloroform and tetrachloroethane) or as a result of reaction with a molecule of isocyanate (chlorination of 1-naphthylisocyanate in carbon tetrachloride).

Previously, during the investigation of the transformations of arylisocyanates under the action of added aluminum chloride, we presented considerations concerning the orienting influence of the isocyanate group during the introduction of new substituents into the aromatic nucleus [5]. The isocyanate and diacylamine groups were on the same level as the halogens, combining the para- and ortho-orientation with deactivation of the aromatic nucleus.

It seemed possible to trace the orienting influence of the isocyanate group in experiments involving the chlorination of isocyanates by raising the temperature. It is well known that at a temperature above 115°, as a consequence of the thermal dissociation of the acid chloride of phenylcarbamic acid, hydrogen chloride does not yield addition products with phenylisocyanate [6], and one could expect substitution here as a result of the direct action of chlorine on arylisocyanate. The chlorination of phenylisocyanate at 120-130° confirmed this hypothesis. The process proceeds many times more slowly than in chloroform at ordinary temperature. Not only mono-, but also polychloro-derivatives, are formed, along with a large quantity of phenylisocyanate which does not react. The phenyl-, 4-chlorophenyl-, 2,4-dichlorophenyl- and 2,4,6-trichlorophenyl-isocyanates were detected in the reaction mixture. It was noted that pure phenylisocyanate, free from traces of N,N'-diphenylurea — a constant admixture formed even on brief contact with moist air — absorbs chlorine appreciably more slowly. The chlorination of phenylisocyanate preparations, free from diphenylurea and containing 1% of this substance, for 6 hours in a strong stream of gaseous chlorine under identical conditions led to a weight increase in the first case of 12.5 and in the second of 29.0%.

The catalytic activity of diphenylurea under these conditions can be explained by a greater chlorination rate of this substance or the product of its reaction with phenylisocyanate — 1,3,5-triphenylbiuret, and the decomposition of the chloro-derivative of the latter with the reformation of diphenylurea and chlorine-substituted phenylisocyanate. The formation of 1,3,5-triphenylbiuret from N,N'-diphenylurea and phenylisocyanate and its thermal decomposition in the starting material has been described in the literature [7]. The possibility of bringing about the process according to the following scheme was confirmed by special experiments:

$$RNCO + R'NHCONHR' \rightarrow RNHCONR'CONHR' \rightarrow RNHCONHR' + R'NCO.$$

Phenylisocyanate was obtained by heating N,N'-diphenylurea with 1- or 2-naphthylisocyanates, and was distilled off from the reaction mixture. It is of interest to note that phenylisocyanate was also obtained by heating acetanilide with 1-naphthylisocyanate. Such an exchange must apparently also be a consequence of the rearrangement of the intermediate compound N-acetyl-N-phenyl-N'-naphthylurea.

In contrast to phenylisocyanate, 1-naphthylisocyanate at 160-170° vigorously absorbs chlorine with the formation of 4-chloro- and 2,4-dichloro-1-naphthylisocyanates and products of more profound chlorination. The rate and direction of the reaction under these circumstances must be explained in connection with the greater stability and reactivity of the nuclear-substituted acid chloride of 1-naphthylcarbamic acid.

EXPERIMENTAL

Reaction of Phenylisocyanate with Chlorine in Chloroform. 10 g of phenylisocyanate was introduced into 80.8 ml of a solution of 5.96 g of chlorine in chloroform. After 12 hours it was filtered, washed with chloroform, and dried in a vacuum desiccator. Colorless crystals were formed; yield 4.57 g.

Found %: HCl 19.07, 19.39. $C_7H_5ONCl_2$. Calculated %: HCl 19.21.

A portion of the substance was introduced into concentrated sulfuric acid, diluted with water, neutralized and steam distilled. M.p. 69.6-70.8°. A mixture with 4-chloroaniline (m.p. 68.8-70.8°) melted at 69.0-70.8°.

Reaction of Isocyanate with Chlorine in Carbon Tetrachloride. 1) A weighed sample of isocyanate (phenyl-4-tolyl-, 4-nitrophenylisocyanate) was placed in a solution of an equimolecular quantity of chlorine in carbon tetrachloride. After about 12 hours the solvent and chlorine were eliminated under a vacuum. The residue did not contain chlorine and consisted of unchanged isocyanate. In the experiment with phenylisocyanate the latter was identified in the form of the methyl ester of phenylcarbamic acid, m.p. 44.4-46.4°; in the experiment with 4-tolylisocyanate — in the form of the butyl ester of 4-tolylcarbamic acid, m.p. 60.4-62.0°; in the experiment with 4-nitrophenylisocyanate — as the same, m.p. 55.6-57.0°.

2) 20.0 g of phenylisocyanate was placed in 165 ml of a solution of 12.09 g of chlorine in carbon tetrachloride and a stream of dry hydrogen chloride was passed over the surface of the solution for 7 minutes. After 12 hours

the colorless crystalline precipitate was filtered, washed with carbon tetrachloride and dried in a vacuum at room temperature. 39.5 g of a substance, identical with the acid chloride of 4-chlorophenylcarbamic acid obtained by conducting the reaction in chloroform solution, was obtained.

3) 46.2 ml of a solution of 3.88 g of chlorine in carbon tetrachloride was added to 9.21 g of 1-naphthylisocyanate at 5°. In 20 minutes a white crystalline precipitate had settled out, which was filtered, pressed out and dried in a vacuum at room temperature. Weight 2.10 g. M.p. 86-89° with decomposition.

Found %: HCl 13.07. $C_{11}H_7ONCl_2$. Calculated %: HCl 15.20.

The methyl ester of 4-chloro-1-naphthylcarbamic acid with m.p. 148.8-149.7° was formed with methyl ether. A mixture with the substance obtained from 4-chloro-1-naphthylisocyanate and methyl alcohol (m.p. 149.3-149.7°) melted at 149.0-149.7°.

Reaction of Phenylisocyanate with Bromine. 20 g of bromine was added in drops to a solution of 10 g of phenylisocyanate in 50 ml of chloroform which was being cooled with an ice mixture. It was filtered, washed with chloroform and dried on a clay plate in a vacuum over potassium hydroxide. 10.23 g of a colorless crystalline substance with m.p. 134-144° (with decomposition [3]) was obtained.

Found %: HBr 27.23, 27.20. $C_7H_5ONBr_2$. Calculated %: HBr 29.03.

A portion of the material was placed while cool in concentrated sulfuric acid, the sulfuric acid solution was poured out on ice, neutralized with alkali and the 4-bromoaniline, m.p. 62.4-63.4° (66° [8]) was steam distilled.

Another portion of the material (0.1 g) was placed in 1 ml of absolute alcohol, and 0.35 g of pyridine was added. The ethyl ester of 4-bromocarbamic acid with m.p. 78.6-79.4° (81° [3]) precipitated during dilution with water. 10 g of the substance was heated for 3 hours at 155-160° and vacuum distilled. 3.1 g of 4-bromophenylisocyanate with m.p. 37-41° (42° [3]) was obtained.

Dry hydrogen bromide was passed into a solution of 4-bromophenylisocyanate in chloroform. The precipitate was filtered, washed, and dried over potassium hydroxide. Colorless crystals with m.p. 135-145° were obtained. A mixture with the substance obtained by the action of bromine on phenylisocyanate, melted at 134-145°.

Chlorination of Phenylisocyanate. 1) With the object of excluding traces of admixed N,N'-diphenylurea or of 1,3,5-triphenylbiuret, 60 g of freshly prepared phenylisocyanate was treated for 1 hour with phosgene at 150°, the temperature was lowered to 120-130° and a strong stream of chlorine was passed into it for 6 hours. The weight of the chlorinated mass was 67.5 g. The following fractions were obtained by distillation: 1st 162-175° (50.6 g); 2nd 175-200° (5.20 g); 3rd 200-247° (7.4 g).

2) 60 g of freshly prepared phenylisocyanate and 0.6 g of N,N'-diphenylurea were chlorinated for 6 hours at 120-130°. The weight of the chlorinated mass was 77.98 g. Distillation yielded the following fractions: 1st 162-175° (32.39 g), 2nd 175-225° (22.54 g) 3rd 225-255° (12.09 g). The following were isolated from the 1st and 2nd fractions by subsequent fractional distillation and crystallization: phenylisocyanate, 4-chlorophenylisocyanate (m.p. 30-32°; it yielded the methyl ester of 4-chlorophenylcarbamic acid, m.p. 114.4-116.8° with methyl alcohol; 4-chloroaniline, m.p. 69.4-70.8° by decomposition with sulfuric acid; and 4-chloroacetanilide, m.p. 176-177° with acetic anhydride), 2,4-dichlorophenylisocyanate (m.p. 57.0-58.8°; it yielded 2,4-dichloroanilide, m.p. 61.4-62.4° by decomposition with sulfuric acid and 2,4-dichloroacetanilide, m.p. 145-146° with acetic anhydride). 2,4,6-Trichloroaniline (m.p. 74.8-75.8°; it yields 2,4,6-trichloroacetanilide, m.p. 205.0-206.6° with acetic anhydride) was isolated from the 3rd fraction after decomposition with sulfuric acid, dilution with water and steam distillation. None of the substances isolated gave melting point depressions with substances obtained by known methods. No amines were detected in the distillate obtained by steam distillation of the sulfamines obtained by the decomposition of the 1st and 2nd fractions with concentrated sulfuric acid, which, according to Beilshtein and Kurbatov [9], indicates the absence of o-chloroaniline.

Chlorination of 1-Naphthylisocyanate. A stream of chlorine was passed into 35.07 g of 1-naphthylisocyanate at 160-170° until the weight became equal to 42 g. Vacuum distillation at 4 mm yielded the following fractions: 1st 138-143° (9.70 g); 2nd 143-156° (14.09 g); 3rd 156-175° (14.76 g). The 1st fraction primarily consisted of 1-naphthylisocyanate, while 4-chloro-1-naphthylisocyanate was isolated from the 2nd fraction by recrystallization from benzene. A portion of the material of the 3rd fraction was placed into concentrated sulfuric acid. A sulfate was isolated by dilution of the sulfuric acid solution with water and ice, from which a substance with a m.p. 79.5-80.5° was obtained by steam distillation in acidic medium; after recrystallization from ethyl alcohol it melted at 80.7-81.7° (m.p. of 2,4-dichloro-1-naphthylamine 82° [10], 83-84° [11]). It yielded an acetyl derivative with acetic anhydride – needles with m.p. 217.9-218.2° (from diluted ethyl alcohol). A mixture with 2,4-dichloro-1-acetylaminonaphthalene, obtained by chlorinating 1-acetylaminonaphthalene (m.p. 217.8-218.5°) melted at 217.9-218.5°. Alkali was added to the portion of the material remaining after separation of the 2,4-dichloro-1-naphthylamine and distillation was resumed. A product with m.p. 93-95° passed over into the distillate. A substance with m.p. 188.9-189.5° was obtained after acetylation with acetic anhydride. A mixture with 4-chloro-1-acetylaminonaphthalene, m.p. 189.5-189.8°, obtained from 1-acetylaminonaphthalene with potassium chlorate, melted at 188.4-188.9°.

Exchange Reaction of Naphthylisocyanate with N,N'-Diphenylurea and Acetanilide 1) 10.6 g of N,N'-diphenylurea and 16.9 g of 1-naphthylisocyanate were heated in a distillation flask. 4.9 g of phenylisocyanate (41.1% of the theoretical quantity, calculating on the basis of the 1-naphthylisocyanate) was distilled off into the receiving flask.

2) 3.91 g of phenylisocyanate (65.7% of the theoretical) was obtained from 10.6 g of N,N'-diphenylurea and 8.45 g of 1-naphthylisocyanate, analogously to the preceding.

3) 1.20 g of phenylisocyanate (50.4% of the theoretical) was obtained from 4.24 g of N,N'-diphenylurea and 3.38 g of 2-naphthylisocyanate.

4) 0.49 g of phenylisocyanate was obtained from 6.75 g of acetanilide and 8.45 g of 1-naphthylisocyanate. The phenylisocyanate was identified in the form of the methyl ester of phenylcarbamic acid.

SUMMARY

1. It was established that, contrary to the data of Gumpert and Curtius, arylisocyanates do not form addition products with chlorine and with bromine.

2. The chlorination of phenyl and 1-naphthylisocyanates was investigated.

3. It was established that phenylisocyanate is obtained by heating 1- and 2-naphthylisocyanates with N,N'-diphenylurea and acetanilide.

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* See Consultants Bureau Translation, page 835.

REACTION OF N,N'-BIS-(HALOMAGNESIUM)-ARYLAMINES WITH ESTERS AND ACID HALIDES

P. A. Petyunin, I. S. Berdinsky and V. S. Shklyaev

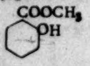
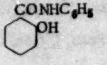
It is well known that organomagnesium derivatives of aromatic amines react with esters of carboxylic acids with the formation of arylamides [1]. This reaction has recently found application for the synthesis of polyenes, for example Vitamin A [2] and the arylamides of β-hydroxy acids [3].

Calculated on the basis of the amount of ester taken, arylamides are obtained in excellent yield, while only half of the quantity of amine taken is converted into arylamide. During the preparation of the arylmagnesium halide-amine, the latter often precipitates and a considerable quantity of dry ether is consumed in order to dissolve it.

As our experiments demonstrated, these drawbacks of the method can readily be eliminated if the reaction is conducted with organodimagnesium derivatives of aromatic amines in accordance with the following scheme:

$$RCOOR' + ArN(MgX)_2 \longrightarrow Mg(OR')X + RC(OMgX){=}NAr \xrightarrow{HCl} MgXCl + RCONHAr.$$

At the same time the N,N-bis-(halomagnesium)-arylamine reacts with the ester group in equimolecular proportions, and thereby guarantees maximum utilization of the amine taken for the reaction.

Experiment No.	Ester	N,N-Bis-(bromomagnesium)-arylamine	Arylamide	Yield (in %)	Melting point	
					our data	according to the literature data [6]
1	$CH_3COOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_3CONHC_6H_5$	83.1•	113-114°	113-114°
2	$CH_3(CH_2)_2COOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_3(CH_2)_2CONHC_6H_5$	81.1	95.5	95- 96
3	$C_6H_5COOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5CONHC_6H_5$	83.3	161-162	162
4	$C_6H_5COOC_2H_5$	β-$C_{10}H_7N(MgBr)_2$	$C_6H_5CONHC_{10}H_7$-β	88.4	160-161	161
5	$C_6H_5COOC_2H_5$	o-$CH_3C_6H_4N(MgBr)_2$	$C_6H_5CONHC_6H_4CH_3$-o	97.3	143-144	142-143
6	$(COOC_2H_5)_2$	$C_6H_5N(MgBr)_2$	$(CONHC_6H_5)_2$	85	244-245	245
7	$C_2H_5OCOCH_2CH_2COOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5NHCOCH_2CH_2CONHC_6H_5$	98.7	222-225	226
8	$C_6H_5CH=CHCOOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5CH=CHCONHC_6H_5$	83.6	151-152	150-151
9	$CH_2ClCOOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_2ClCONHC_6H_5$	71.5	133	134-135
10	$(C_6H_5)_2C(OH)COOC_2H_5$	$C_6H_5N(MgBr)_2$	$(C_6H_5)_2C(OH)CONHC_6H_5$	78.4	174-175	175 [4]
11				37.7	135-136	134-135

It should be noted that the application of organodimagnesium amine derivatives for the indicated purpose has not been described in the literature.

We conducted a reaction between $ArN(MgBr)_2$, where Ar = C_6H_5, o-$CH_3C_6H_4$ and β-$C_{10}H_7$, on the one hand and the esters of mono- and dibasic acids and their derivatives, on the other hand.

•In all the experiments, the yield of arylamide was calculated on the basis of the amine taken for the reaction.

Methods. Ethylmagnesium bromide was obtained from 0.05 mole of ethyl bromide and 0.05 mole of magnesium in 25 ml of ether. An ethereal solution of 0.025 mole of aromatic amines was added to the latter while it was being stirred. After evolution of ethane the reaction mass was heated on a water bath for 30 minutes. At the same time the organomagnesium amine derivative (ArNHMgBr) which was being formed reacted with ethylmagnesium bromide and N,N-bis-(bromomagnesium)-arylamine was obtained. At the end of the reaction the vigorous evolution of ethane changed to regular boiling of the ether.

A solution of 0.025 mole of the carboxylic acid ester in 10-20 ml of ether was added to an ethereal solution of 0.025 mole of N,N-bis-(bromomagnesium)-arylamine. The reaction mass was decomposed with 10% hydrochloric acid after having been heated for 30 minutes on the water bath and the arylamide which formed was isolated by the usual method.

The experimental results are presented in the table.

It is evident from the tabular data that the yield of arylamides based on the amount of amine taken for the reaction amounts to 7.15-98.7% of the theoretical.

The anilide of salicyclic acid which was obtained in a yield of 37.7% (Experiment 11) appears to be an exception. This is to be explained by the fact that the labile hydrogen of the salicylic ester phenol group decomposes the N,N,bis-(bromomagnesium)-arylamine, converting it into arylbromomagnesium amines.

The dibenzoyl derivatives of aromatic amines were obtained in excellent yields by the action of N,N-bis-(bromomagnesium)-arylamines on benzoyl chloride. The reaction proceeds according to the following scheme:

$$ArN(MgBr)_2 + 2C_6H_5COCl \longrightarrow ArN(COC_6H_5)_2 + MgBr_2 + MgCl_2.$$

Method. 0.05 mole of benzoyl chloride was added to 0.025 mole of N,N-bis-(bromomagnesium)-arylamine, obtained as indicated above. The reaction mass was heated for 1.5 hourson a water bath and then decomposed with 10% hydrochloric acid. The dibenzoyl amine derivative was isolated from the ethereal layer after elimination of the solvent.

Dibenzoyl-o-toluidine was obtained in a yield 91.1% of the theoretical. M.p. 109-110°. Literature data: 111-112° [5]. Dibenzoylaniline was obtained in a yield 74.2% of the theoretical. M.p. 160-161°. According to the literature data, dibenzoylaniline melts at 160-161° [6].

SUMMARY

1. The reaction of N,N-bis-(halomagnesium)-arylamines with esters and acid halides was studied. It was thereby established that N,N-bis-(halomagnesium)-arylamines react like organodimagnesium compounds.

2. It was established that the reaction between esters and N,N-bis-(halomagnesium)-arylamines has a number of advantages in comparison with arylhalomagnesiumamines and can be recommended for the synthesis of arylamines of mono- and dibasic acids, and of halogen-, hydroxy- and α,β-unsaturated acids.

3. The example of the reaction of N,N-bis-(bromomagnesium)-phenyl- and o-tolylamines with benzoylchloride demonstrated the possibility of applying this reaction for the synthesis of dibenzoyl derivatives of aromatic amines.

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* See Consultants Bureau Translation, page 1033.

STERIC HINDRANCE AND PROPERTIES OF CERTAIN ARYLAMINONAPHTHOQUINONES

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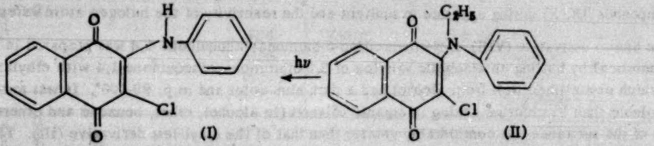
It was recently shown by us that 2-anilino-3-chloronaphthoquinone-1,4 ("the ethyl-less derivative") (I) and 2-N-ethylanilino-3-chloronaphthoquinone ("the ethyl derivative") (II) differ significantly from each other [1]. This difference in the ethyl derivative (II) in comparison with compound (I) is manifested: 1) in the markedly changed color and displacement toward the short waves of the absorption maximum; 2) in the lower melting point; 3) in the considerably greater solubility in organic solvents; 4) in the lower stability toward alkalis and 5) in the increased sensitivity of solutions to the action of light (see the table).

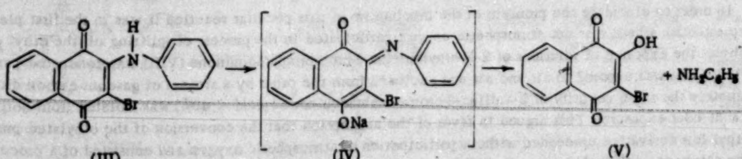


(I) (II)

Such a marked difference in the properties of substances (I) and (II) was explained by the peculiarities in the chemical structure of their molecules; specifically, in the presence of steric hindrance in the ethyl derivative. The study of stereochemical models of compounds (I) and (II) demonstrated that the phenyl radical in the ethyl derivative (II), thanks to the presence of a halogen atom in the ortho position, is displaced from the plane occupied by it in the ethyl-less derivative (I) and has limited possibility of rotation.

The behavior of the ethyl derivative in sunlight turned out to be particularly interesting. Even after brief irradiation the violet color of an alcohol solution is converted into red and then into orange. A red crystalline product was obtained from the solution in a yield of ~60% after it had been concentrated, and turned out to be the "ethyl-less derivative" (I). A characteristic photochemical reaction consequently proceeds during exposure to sunlight in which cleavage of the ethyl group from the nitrogen atom and conversion of the initial substance (II) into 2-anilino-3-chloronaphthoquinone (I) takes place.

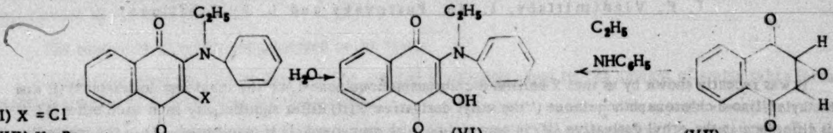
The behavior of substances (I) and (II) toward alcoholic alkali is no less interesting. Miller in Markovnikov's laboratory [2] had already observed that 2-anilino-3-bromonaphthoquinone-1,4 (III) is readily hydrolyzed by alcoholic alkali, with the formation of 2-hydroxy-3-bromonaphthoquinone-1,4 (V). Evidently, an orthoquinoid tautomer with an arylimine bond (IV) appears here as in intermediate product. The instantaneous conversion of the orange color of a solution of the substance in alcohol into dark violet during addition of alkali argues in favor of this. After a short time the solution becomes brown and the hydroxy product (V) precipitates from it on acidification:



(III) (IV) (V)

The chloro derivative (I) acts in exactly the same way as the bromo derivative. It is smoothly hydrolyzed into 2-hydroxy-3-chloronaphthoquinone-1,4.

Such tautomerism is naturally impossible in the 2-N-ethylanilino-3-chloronaphthoquinone (II) and hydrolytic cleavage of the arylamino group does not take place. However, the presence of steric hindrance in the ethyl derivative influences the properties of the halogen atom. The latter acts as though it were aliphatic in its character and is readily replaced by the hydroxyl group, yielding a new derivative, the 1,4-naphthoquinone (VI). The substance with the structure (VI) was synthesized from 2,3-hydroxy - ,4-naphthoquinone (VII) [4] and ethylaniline; it turned out to be identical with the hydrolysis product of the ethyl derivative.



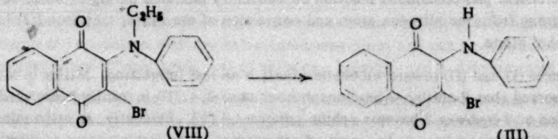
II) X = Cl
VIII) X = Br
(VI)
(VII)

It was of interest to consider the properties of the related compounds in which the steric hindrance should be approximately the same as in the 2-N-ethylanilino-3-chloroderivative.

In connection with this the behavior of the 2-N-ethylanilino-3-bromo derivative (VIII) and also of the acetylated compounds (IX, X) during exposure to sunlight and the reactivity of the halogen atom werestudied.

The bromo derivative (VIII), 2-N-ethylanilino-3-bromonaphthoquinone-1,4 was prepared in a yield of 80-85% of the theoretical by boiling an alcoholic solution of 2,3-dibromonaphthoquinone-1,4 with ethylaniline. This product, which crystallized well from alcohol, had a dark blue color and m.p. 99-100°. It was somewhat more difficultly soluble than its chlorine analog in organic solvents (in alcohol, ether, benzene and others), however, the solubility of the substance was considerably greater than that of the ethyl-less derivative (III). The bromo derivative (VIII) was very similar to the chlorine analog (II) in its properties. Thus, the bromine atom in its molecule was also distinguished by a great lability, and during reaction with alcoholic alkali was replaced readily, almost quantitatively, by the hydroxyl group. Even in the cold the violet alcoholic solution of substance (VIII) rapidly became brown during the addition of NaOH solution. A dark-blue precipitate settled out during the acidification of such a solution with hydrochloric acid, and consisted of the above-mentioned 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4 (VI).

During the exposure of an alcoholic solution of 2-N-ethylanilino-3-bromonaphthoquinone-1,4, the cleavage of the ethyl group and formation of 2-anilino-3-bromonaphthoquinone (III) occurs:



(VIII)
(III)

Consequently, both for the chloro derivative (II) and for the bromine analog (VIII) with a noncoplanar structure of the molecule, there takes place this peculiar photochemical reaction with splitting off of the $-C_2H_5$ group and formation of a substance with greater possibilities of planar arrangement of groups.

In order to elucidate the problem of the mechanism of this peculiar reaction it was in the first place necessary to establish whether or not atmospheric oxygen participated in the process of splitting off the ethyl group. With this object the exposure of solutions of 2-N-ethylanilino-3-bromonaphthoquinone (VIII) was conducted parallelly in two flasks; one was exposed to air and air was excluded from the other by a stream of gaseous carbon dioxide. Approximately the same quantity of 2-anillino-3-bromonaphthoquinone (yield ~ 40%) was isolated from both solutions after a 30-hour exposure. This argued in favor of the assumption that the conversion of the ethylated product into the ethyl-less derivative proceeded without participation of atmospheric oxygen, and consisted of a process involving the cleavage of the ethyl group in which, possibly reduction occurs more rapidly than oxidation*.

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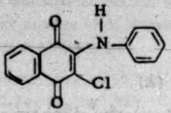
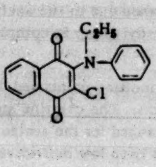
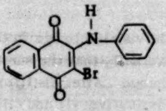
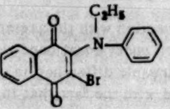
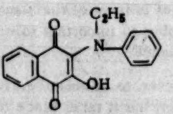
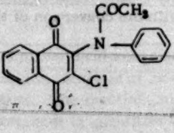
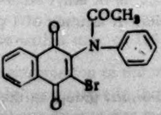
*The mechanism of this characteristic photoreaction should be studied in still greater detail.

Properties of Naphthoquinonephenylamines, Unsubstituted and Substituted at the Nitrogen Atom

Experiment No.	Formula	Color		Melting point (in °)	Solubility in benzene	$E_{1/2}$* (in volts relative to a calomel electrode	Reactivity of the halogen atom
		of the crystals	of an alcoholic solution				
1		Red	Orange	208-210	Very difficultly soluble	−0.245	Inert
2		Reddish Brown	Violet	94- 95	Very excellently soluble	−0.152	Reactive
3		Red	Orange	194-195	Difficultly soluble	−0.245	Inert
4		Dark Violet	Violet	99-100	Quite soluble	−0.150	Reactive
5		Blue	Blue	151-152	Quite soluble	−0.298	—
6		Yellow	Bright Orange	134-135	Quite soluble	−0.108	Reactive (replaced by the amino group)
7		Dark Yellow	Yellow	142-143	Quite soluble	−0.105	Reactive (replaced by the amino group)

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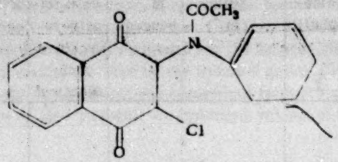
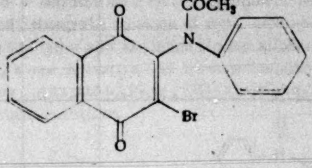
* The polarographic investigations were conducted in a buffer solution of 0,1 N CH_3COONa and 0,1 N CH_3COOH in 75% alcohol.

The properties of acetyl derivatives were further studied and specifically, the properties of 2-N-acetylanilino-3-chloronaphthoquinone (IX) [5] and 2-N-acetylanilino-3-bromonaphthoquinone (X):



(IX)



(X)

The latter substance, not described in the literature, was prepared by the acetylation of the bromo derivative (III) with acetic anhydride in the presence of concentrated sulfuric acid.

As was demonstrated by stereochemical models, the space occupied by the COCH$_3$ group is approximately equal to that occupied by the C$_2$H$_5$ group. In connection with this, the steric hindrance due to the acetyl group in compounds (IX) and (X) should be approximately equal to that which is due to the ethyl group in compounds (II, and VIII).

Actually, the acetyl derivatives, similarly to the ethyl derivatives, have low melting points and differ considerably in their greater solubility in organic solvents from the unsubstituted products. The chlorine atom of compound (IX) is known to have considerable reactivity (for example, it is readily exchanged for the amino group [5]), in contrast to the free compound (I). Like the ethyl derivatives, the acetyl products have low half-wave potentials, (see the table). However, the acetyl products (IX, X) are markedly different in the color of their crystals and solutions from those of the ethyl products (II and VIII) — they are yellow colored.

Exposure of solutions of these substances to sunlight did not evoke appreciable visible change in their color (the orange color of the solution only became slightly brighter) and it appeared externally that the substances had not changed. It turned out, actually that the substances had undergone profound change. After distilling off the solvent we succeeded in isolating a small quantity of the corresponding ethyl-less derivatives (I) and (II). Among the decomposition products of the acetyl derivatives, the presence of ammonia and halogen derivatives which exhibited the halide ion reactions were detected qualitatively.

The investigation thus demonstrated that, with the acetyl products, in connection with the presence of steric hindrance, a characteristic cleavage takes place during exposure to sunlight which under equal conditions proceeds more profoundly than with the ethyl derivatives. This circumstance and the noticeable difference in color in comparison with the ethyl derivatives (II) and (VIII) (see the table) may be associated with the fact that in the acetyl derivatives the unshared electron pair at the nitrogen atom is displaced in the direction of the carbonyl of the acetyl group and has less possibility of interaction with the quinoid ring.*

Comparison of the properties of the N-ethyl- and N-acetyl derivatives argues in favor of the assumption that unshared electron pairs, present in our case on the nitrogen and halogen atoms, play an important role in the complex interrelationships of groups and atoms caused by the presence of steric hindrance.

The stability of the ethyl-less derivative (I) during exposure, appears, however, to be relative. A gradual change in the ethyl-less derivative is also observed under the influence of sunlight, but it takes place to a considerably smaller extent than in the case of exposure of the N-ethyl derivative. The light sensitivity of 2-anilino-3-chloronaphthoquinone has, however, other causes and is apparently associated with the conversion of the paraquinone into orthoquinones (IV).

EXPERIMENTAL

Preparation of 2-N-Ethylanilino-3-bromonaphthoquinone-1,4

1 g (0.003 mole) of 2,3-dibromonaphthoquinone [2] which was dissolved in 220 ml of ethyl alcohol by heating on a water bath, was placed in a round bottom flask supplied with a reflux condenser. A solution of 1 g of freshly prepared ethylaniline in 5 ml of alcohol was poured into the hot solution.

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* Compare the observations of Levkoev, Sveshnikov and Barvin on the role of acyl-amino groups in the color of thiocarbocyanines with steric hindrance [6].

The mixture was heated on a water bath for 24 hours. The orange solution gradually became violet. After the dark violet solution obtained had been cooled, it was filtered off from the insignificant quantity of unreacted dibromonaphthoquinone. The alcohol was completely driven off and 15 ml of hydrochloric acid (1:4) was poured into the dark violet colored liquid which remained, to remove unreacted ethylaniline.

100 ml of ethyl ether was added to the mixture to extract the violet product. The ether was driven off and the resinous mass which remained was dissolved by heating in 50 ml of ethyl alcohol; on cooling, a precipitate settled out in the form of violet crystals (consisting under the microscope of green translucent rhombohedra). The precipitate was filtered off and dried. The yield of product was 1.0 g (87%) with a m.p. of 98-99°. The melting point did not change after recrystallization. The product was readily soluble in alcohol, benzene, ether and chloroform, giving a violet color.

4.390 mg sub.: 0.157 ml N_2 (23°, 724 mm). 0.0733 g sub.: 0.0383 g AgBr (Carius). Found %: N 4.09, Br 22.23. $C_{18}H_{14}O_2NBr$. Calculated %: N 3.93; Br 22.26.

Hydrolysis of 2-N-Ethylanilino-3-bromo- and 3-Chloronaphthoquinone-1,4

0.36 g (0.001 mole) of 2-N-ethylanilino-3-bromonaphthoquinone was dissolved in 20 ml of alcohol. 1 ml of 30% NaOH solution was added to the violet solution. The solution rapidly began to change color and after 20-30 minutes acquired a brown color. After 30 minutes the solution was acidified with 10 ml of a 2N HCl solution, whereupon the color of the solution changed to blue and a crystalline blue precipitate settled out. The reaction mass was diluted with 20 ml more of water and left for 2 hours until the precipitate had entirely settled out. After this, the precipitate was filtered off, washed free of acid with water and dried. The weight of the precipitate was 0.27 g (93%), m.p. 150-151°.

When mixed with 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4, the hydrolysis product obtained did not depress the melting point.

The hydrolysis of 1-N-ethylanilino-3-chloronaphthoquinone-1,4[*] was conducted analogously. In this case 0.26 g (90%) of a blue crystalline product with a m.p. of 150-151°, which was identical with 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4 was isolated from 0.32 g (0.001 mole).

Preparation of 2-N-Ethylanilino-3-Hydroxynaphthoquinone-1,4

0.88 g (0.005 mole) of 2,3-dihydroxynaphthoquinone-1,4 [4] was heated to boiling with 5 ml of ethyl alcohol. 0.54 g of ethylaniline was added to the solution. The color of the solution became dark violet. After having been boiled for 9 hours the solution was cooled, the precipitate which settled out was filtered off and washed with dilute hydrochloric acid, water and with alcohol. The weight of the precipitate was 0.7 g and the m.p. 148°. The precipitate was recrystallized from 10 ml of alcohol. The weight was 0.5 g (34%), m.p. 151-152°, which did not change after recrystallization. The product consisted of blue needle like crystals. It was very readily soluble in alcohol and in glacial acetic acid. It dissolved in alkalis, yielding a brown color. It dissolved in concentrated H_2SO_4, giving a rose color. It separated unchanged when the solution was diluted.

4.630 mg sub.: 0.194 ml N_2 (18°, 740 mm). 6.170 mg sub.: 0.267 ml N_2 (18°, 747 mm). Found %: N 4.79, 4.95. $C_{18}H_{15}O_3N$. Calculated %: N 4.77.

Behavior of 2-N-Ethylanilino-3-chloro- and 2-N-Ethylanilino-3-bromonaphthoquinone on Illumination with Sunlight[**]

1.50 mg of 2-N-ethylanilino-3-chloronaphthoquinone was dissolved in 100 ml of ethyl alcohol in a quartz flask. The flask with the violet solution (reddish tinge) was placed in sunlight for approximately 60 hours. Even after the first 20 hours of exposure there was a noticeable change of the violet color into reddish, which lost color and became orange with a brown tint. After the conclusion of the illumination there was a rather distinctly perceptible isonitrile odor in the alcoholic solution (there was no acetaldehyde odor). The alcohol was driven off and the volume reduced to 5 ml, and the brownish-red solution was left to cool. The fine red crystalline precipitate which settled out was washed with a small quantity of alcohol and dried. The weight of the precipitate was 16 mg, and the m.p., 205-207° (208-210° according to the literature data). About 3 mg more of the red product (impure) was isolated from the mother liquor.

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[*] 2-N-Ethylanilino-3-chloronaphthoquinone-1,4 was prepared according to the data of reference [3]. Nothing was stated concerning the yield of product in the latter. The substance was obtained in small yields (around 10-20%) in our experiment. The reaction proceeded considerably more slowly than in the case of the bromo derivative.

[**] Both substances in quantities of 50 mg and 57 mg respectively were dissolved in 100 ml of alcohol and were subjected in closed quartz flasks to 130 hours exposure to a quartz lamp (1 kW at a distance of 60 cm). After this period the solutions became light brown with a brown tint. 10 mg of the red chloride with a m.p. of 196-200° and 8 mg of impure bromide with a m.p. of 166-170° could be isolated from the solutions.

After evaporation of the mother liquors a resinous brownish-yellow residue remained. The odor of acetaldehyde was distinctly perceptible in the solution. In the given case, apparently, a considerable portion of the ethyl-less products which were formed was more profoundly decomposed in the exposure process than during exposure to direct sunlight.

The crystalline product was identified as 2-anilino-3-chloronaphthoquinone (a mixed sample did not cause depression of the melting point; polarograms of alcohol solutions of the synthetic product and the product of the photochemical cleavage were identical).

2. The experiment with 2-N-ethylanilino-3-bromonaphthoquinone was conducted under the same conditions as with the chlorine analog. 57 mg of the product under investigation was dissolved in 100 ml of alcohol in a quartz flask. Change of the violet color into red proceeded even after 20 hours of exposure. During further exposure the color of the solution gradually became paler, and at the end of the exposure became brownish-orange (somewhat darker than for the chlorine analog). The solvent was then driven off to a volume of 3 ml. A red crystalline product precipitated on cooling. The latter was filtered off, washed with alcohol and dried. The weight of the product was 17 mg, m.p. 189-191°. A mixed sample with 2-anilino-3-bromonaphthoquinone had a m.p. of 190-191°, i.e., caused no melting point depression.

In a control experiment where the solution was in a carbon dioxide atmosphere, the results were analogous. 57 mg of 2-N-ethylanilino-3-bromonaphthoquinone-1,4 was taken for the exposure and 16 mg of 2-anilino-3-bromonaphthoquinone with a m.p. of 187-190° was obtained. During a 16 hour exposure during which the violet color of the solution changed into red, 28 mg of a red crystalline product with a m.p. of 176-177°, after recrystallization – m.p. 190-192° – was isolated.

Preparation of the 2-N-Acetylanilino-3-chloronaphthoquinone

The acetyl derivative was obtained by the acetylation of 2-anilino-3-chloronaphthoquinone with acetic anhydride with the addition of concentrated sulfuric acid [5]. It was a yellow crystalline product with a m.p. of 134°.

Preparation of 2-N-Acetylanilino-3-bromonaphthoquinone-1,4

The product was obtained by the acetylation of 2-anilino-3-bromonaphthoquinone-1,4 with acetic anhydride (in the presence of a small quantity of strong H_2SO_4). 0.98 g (0.003 mole) of 2-anilino-3-bromonaphthoquinone-1,4 was taken for the experiment. 0.53 g (50%) of the acetyl derivative with a m.p. of 140-141° was obtained. The m.p. after recrystallization was 142-143°. The substance was readily soluble in alcohol, benzene, glacial acetic acid, chloroform, in contrast to the starting material which was difficultly soluble in these solvents.

6.570 mg sub.: 0.196 ml N_2 (22°, 735 ml). Found %: N 3.97. $C_{18}H_{12}O_3NBr$. Calculated %: N 3.78.

Behavior of 2-N-Acetylanilino-3-chloronaphthoquinone (IX) and 2-N-Acetylanilino-3-bromonaphthoquinone (X) in Sunlight

1. 52 mg of 2-N-acetylanilino-3-chloronaphthoquinone, dissolved in 100 ml of alcohol (orange solution), was subjected to exposure for 60 hours. Even in the first 10-15 hours the color of the solution became lighter; thereafter, it remained unchanged visually.

The alcohol was driven off until the volume was reduced to 3 ml. The dark orange solution was cooled. ~ 3 mg of a red crystalline product with a m.p. of 204-205° precipitated, which appeared to be 2-anilino-3-chloronaphthoquinone. After concentrating the mother liquor a vitreous dark yellow mass remained from which the individual substances could not be isolated.

The presence of ammonium salts and Cl ions was detected qualitatively.

2. 59 mg 2-N-acetylanilino-3-bromonaphthoquinone, dissolved in 100 ml of alcohol, was subjected to exposure to light in an analogous manner. The solution was light orange and its color was not appreciably changed in the exposure process. After distilling off the solvent to a volume of 3 ml, 1.2 mg of 2-anilino-3-bromonaphthoquinone with a m.p. of 180-183° (impure) was isolated from the cooled solution. The filtrate was concentrated further to a volume of 1 ml and again cooled. Only a very insignificant quantity of the bromoanilide precipitated as a result of this. No other products could be isolated.

A strong odor of ammonia was perceived during the alkalinization of the aqueous residue after ether extraction and the presence of the Br ion was detected qualitatively.

SUMMARY

1. The behavior under the action of light of the N-ethylated and N-acetylated derivatives of 2-anilino-3-halonaphthoquinone-1,4 was studied. The ethylated and acetylated products split off the ethyl or acetyl group during

the action of sunlight and are converted into the unsubstituted products. The reactivity of the halogen atom in position 3 was also characteristically increased in the ethylated and acetylated compounds.

2. The photochemical cleavage of groups at the nitrogen atom and also the increased reactivity of the halogen atoms in the ethylated and acetylated products were explained by the presence in their molecules of steric hindrance due to the adjacent positions of the halogen atom and the N-ethylaniline radical in the quinoid ring of naphthoquinone.

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* See Consultants Bureau Translation, page 997.

SYNTHESIS AND REACTIONS OF 3,4-DIKETONES OF THE TETRAHYDROFURAN SERIES

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The 3,4-diketones of the tetrahydrofuran series constitute a very interesting but slightly studied class of compounds. There are no good general methods for the synthesis of these diketones, and only a few of these compounds have been described.

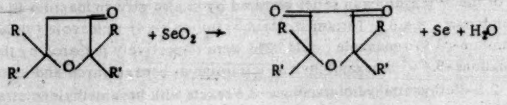
Dupont [1] established in 1913 that during the distillation of 4-nitro-2,2,5,5-tetramethyltetrahydrofuranone-3, along with other reaction products there is formed "a red liquid, boiling around 170°. Left in the moist air it is converted into a white crystalline mass, which melts around 80° after drying and is converted into a red liquid". Dupont deduced from his analytical data that the white crystalline substance was apparently the dihydrate of 2,2,5,5-tetramethyltetrahydrofurandione-3,4. In 1949 this same author [2] showed that during the dehydration of 2,5-dimethylhexandiol-2,5-dione-3,4 with the aid of phosphorus pentoxide, 2,2,5,5-tetramethyltetrahydrofurandione-3,4 is formed, which was characterized by preparing the dioxime, the mono-2,4-dinitrophenylhydrazone, and the quinoxaline from it.

In 1930 T. I. Temnikova and P. A. Tikhomolov [3] established that 2,2,5,5-tetra-o-tolyltetrahydrofurandione-3,4 is formed in a yield of 42% of the theoretical by the oxidation of tetra-o-tolylbutynediol with chromic anhydride in acetic acid.

It was later shown [4] that under analogous conditions tetraphenylbutynediol is converted into 2,2,5,5-tetraphenyltetrahydrofurandione-3,4 (yield 51%). Both these diketones have a bright raspberry color. They were characterized by preparing the monophenylhydrazone, the monooxime and the quinoxaline.

It is well known that α-diketones, α-dialdehydes and α-ketoaldehydes are obtained in excellent yields during the selenium dioxide oxidation of ketones or aldehydes containing a methyl or methylene group in the α-position to the carbonyl group [5]. However, this method, well worked out for the synthesis of α-diketones of the aliphatic, aliphatic-aromatic and alicyclic series, has not been employed for the synthesis of α-diketones of a heterocyclic series.*

The oxidation with selenium dioxide of two ketones of the tetrahydrofuran series – 2,2,5,5-tetramethyltetrahydrofuranone-3 and 2,5-dimethyl-2,5-diethyl-tetrahydrofuranone-3 – was studied in the present work. These ketones were chosen because there is only one methylene group close to the carbonyl group in them and, consequently, their oxidation should lead to only one reaction product:



1) $R = R' = CH_3$
2) $R = CH_3$; $R' = C_2H_5$

We established that during the oxidation of 2,2,5,5-tetramethyltetrahydrofuranone-3 and 2,5-dimethyl-2,5-diethyltetrahydrofuranone-3 with selenium dioxide in dioxane at 100° for 10 hours, 2,2,5,5-tetramethyltetrahydrofurandione-3,4 (yield 83.5% of the theoretical) and 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 (yield 86.5% of the theoretical) were respectively obtained.

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 consists of a crystalline substance (m.p. 54-56°), bright raspberry colored, which is converted into a white dihydrate (m.p. 74-75°) in air. 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 is a bright raspberry colored liquid with a b.p. of 93-95° (15 mm), which does not add water in air, but which is hydrated to give colorless solutions when dissolved in water.

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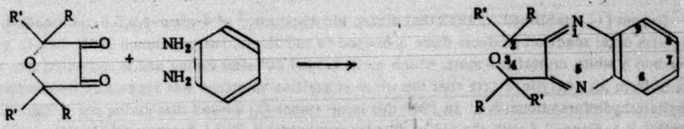
* In Richet's work [6], "Halogen Derivatives of 2,2,5,5-tetramethyltetrahydrofuranone-3" it is mentioned that 2,2,5,5-tetramethyltetrahydrofurandione-3,4 is formed by the oxidation of 2,2,5,5-tetramethyltetrahydrofuranone-3 with selenium dioxide. However, neither the conditions under which the experiment was conducted, nor the yields of reaction products, nor the constants of the reaction are set forth in the work.

In the present work a suitable preparative method was thus worked out for the preparation of diketones of the tetrahydrofuran series in which there are tertiary carbon atoms in positions 2 and 5, and ketone groups in positions 3 and 4.

The diketones prepared by us gave all the characteristic reactions for *a*-diketones. Thus, the dioxime (yield 84%) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 was prepared by the action on the latter of hydroxylamine hydrochloride in water-alcohol solution.

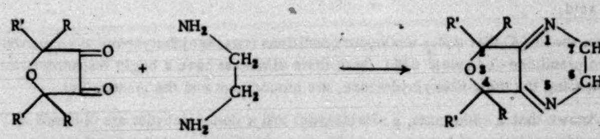
The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 (yield 50%) was also obtained.

Like all *a*-diketones, *a*-dialdehydes and *a*-ketoaldehydes, the diketones obtained by us readily react with o-phenylenediamine to give quinoxalines – 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline (yield 85%) and 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline (yield 86%):



1) $R = R' = CH_3$; 2) $R = CH_3$; $R' = C_2H_5$

The diketones prepared by us reacted vigorously with ethylenediamine to form dihydropyrazines.



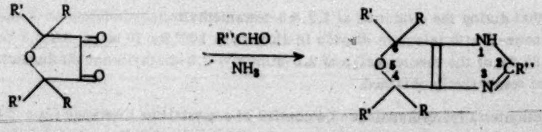
1) $R = R' = CH_3$; 2) $R = CH_3$; $R' = C_2H_5$

2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine was prepared in a yield of 81% of the theoretical and 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine – in a yield of 78% of the theoretical.

Radzishevsky [7] established as early as 1882 that the reaction of *a*-dialdehydes or *a*-diketones with ammonia and aldehydes can surve as an excellent method of synthesis for various imidazoles.

The diketones of the tetrahydrofuran series prepared by us also give imidazoles in excellent yields on reaction with aldehydes and ammonia. 4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole (yield 70%) and 2-phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole (yield 82%) were respectively prepared by the reaction of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 with hexamethylene-tetramine or benzaldehyde and ammonia.

2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 reacts with hexamethylenetetramine and ammonia to give 4,6-dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole (yield 80%):



1) $R = R' = CH_3$; $R'' = H$; 2) $R = R' = CH_3$; $R'' = C_6H_5$; 3) $R = CH_3$; $R' = C_2H_5$; $R'' = H$

The 3,4-diketones of the tetrahydrofuran series can thus serve as convenient starting materials for the synthesis of condensed heterocyclic systems, the structure of which includes the tetrahydrofuran and the quinoxaline, dihydropyrazine or the imidazole rings.

EXPERIMENTAL

1. Synthesis of 3,4-Diketones of the Tetrahydrofuran Series

A. Preparation of 2,2,5,5-Tetramethyltetrahydrofurandione-3,4. A solution of 14.2 g (0.13 mole) of selenium dioxide in 200 ml of moist dioxane was placed in a half liter three-necked flask supplied with a mechanical stirrer with a mercury seal, a dropping funnel and a reflux condenser. The solution was heated to boiling and 14.2 g (0.1 mole) of 2,2,5,5-tetramethyltetrahydrofuranone-3* was added dropwise. The solution was boiled and stirred for 10 hours. The selenium which precipitated was filtered off and the dioxane was distilled off from the solution. In all 8.5 g of selenium (94.5% of the selenium dioxide introduced) was isolated. The residue was dissolved in 200 ml of ether, neutralized with a saturated solution of sodium bicarbonate and washed with water. After driving off the ether from the ethereal solution which had been dried with roasted sodium sulfate, the residue was vacuum distilled; b.p. 85-86.5° (30 mm). The yield was 13 g (83.5%).

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 consisted of bright raspberry colored crystals; m.p. (after sublimation in a sublimator in the presence of phosphorus pentoxide) 54-56°; b.p. 85-85.5° (30 mm); quite soluble in ether and isooctane.

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 rapidly absorbs moisture in air and is converted into the white dihydrate with m.p. of 74-75° (after twofold recrystallization from water).

The dihydrate loses water on heating and is converted into a raspberry colored liquid. The white crystals of the dihydrate give a raspberry coloration to solutions in ether, alcohol and petroleum ether.

Found %: C 50.42, 50.37; H 8.59, 8.48. $C_8H_{12}O_3 \cdot 2H_2O$. Calculated %: C 49.98; H 8.99.

Literature data for 2,2,5,5-tetramethyltetrahydrofurandione-3,4: red liquid, b.p. 170°; m.p. of the white dihydrate around 80° [1].

B. Preparation of 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4. 15 g (0.088 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofuranone-3** was oxidized with 15 g (0.136 mole) of selenium dioxide, as in the preceding experiment. After twofold vacuum distillation, 14 g (86.5%) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 was obtained: b.p. 93-95° (15 mm); m.p. −12.2 to −11.8°; n_D^{20} 1.4422; d_4^{20} 1.0062; MR_D 48.48; calc. 47.85.

Found %: C 65.41, 65.63; H 8.98, 8.81. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75.

2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 consisted of a bright raspberry colored liquid, quite soluble in alcohol, ether, dioxane and isooctane; 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 yielded colorless solutions when dissolved in water.

2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 had not been described in the literature.

2. Preparation of the Dioximes of 3,4-Diketones of the Tetrahydrofuran Series

A. The Dioxime of 2,2,5,5-Tetramethyltetrahydrofurandione-3,4. 1.8 g (0.36 mole) of hydroxylamine hydrochloride was added to a solution, cooled to 0°, of 0.8 g (0.005 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 in a mixture of 15 ml of water and 25 ml of ethyl alcohol, and a solution of 2.3 g of potassium hydroxide in 10 ml of water was then added. The reaction mixture was heated for 2 hours on a water bath and then cooled and saturated with solid carbon dioxide. The precipitate which formed was filtered off and recrystallized from absolute ethyl alcohol. 0.8 g (84%) of the dioxime of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 was obtained which melted at 224-225° after repeated recrystallization.

Found %: N 15.12, 15.18. $C_8H_{14}O_3N_2$. Calculated %: N 15.06.

The literature data for the dioxime of 2,2,5,5-tetramethyltetrahydrofurandione-3,4: volatilizes without melting at 240° [1]; volatilizes without melting at 210° [2].

B. The Dioxime of 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4. The method was analogous to the preceding. The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 was obtained from 1.8 g (0.01 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 3.64 g (0.052 mole) of hydroxylamine hydrochloride: m.p. 193° (after recrystallization from aqueous ethyl alcohol). The yield was 1 g (50%).

Found %: N 13.11, 12.97. $C_{10}H_{18}O_3N_2$. Calculated %: N 13.06.

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* 2,2,5,5-Tetramethyltetrahydrofuranone-3 was synthesized by simultaneous hydration and dehydration of 2,5-dimethylhexyne-3-diol-2,5 in the presence of mercuric sulfate [1]: b.p. 149-149.5° (762 mm); n_D^{20} 1.4202; d_4^{20} 0.9249; MR_D 38.91; calc. 38.69.

** 2,5-Dimethyl-2,5-diethyltetrahydrofuranone-3 was prepared by the simultaneous hydration and dehydration of 3,6-dimethyloctyne-4-diol-3,6 in the presence of mercuric sulfate: b.p. 90-91° (25 mm); n_D^{20} 1.4383; d_4^{20} 0.9319; MR_D 47.97; calc. 47.90.

The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 had not been described in the literature.

3. Preparation of the Quinoxalines of 3,4-Diketones of the Tetrahydrofuran Series

A. Preparation of 2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-quinoxaline. A mixture of 0.4 g (0.0025 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 and 0.25 g (0.0023 mole) of o-phenylenediamine was heated in a test tube until it melted. After the yellow crystalline mass which formed on cooling had been recrystallized twice from alcohol, 0.4 g (85%) of 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline with a m.p. of 101.5° was obtained.

Found %: N 12.43, 12.29. $C_{14}H_{16}ON_2$. Calculated %: N 12.27.

Literature data for 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline [2]: m.p. 98-99°.

B. Preparation of 2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline. A mixture of 0.9 g (0.005 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 0.5 g (0.0046 mole) of o-phenylenediamine was heated in a test tube for 10-15 minutes. After the dark crystalline mass which formed on cooling had been recrystallized twice from ethyl alcohol, 1 g (86%) of 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline was obtained: m.p. 110-111.5°.

Found %: N 10.83, 10.69. $C_{10}H_{20}ON_2$. Calculated %: N 10.52.

2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline had not been described in the literature.

4. Preparation of Dihydropyrazines from 3,4-Diketones of the Tetrahydrofuran Series

A. 2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine. 3.12 g (0.04 mole) of ethylenediamine monohydrate was added to 6.2 g (0.04 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4. The reaction was accompanied by strong evolution of heat and a change in the color from red to yellow. The reaction mass was diluted with ether and dried with roasted potash. After distilling off the ether and twofold vacuum distillation, 5.8 g (81%) of 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine was obtained: b.p. 75.5-75.7° (9 mm); n_D^{20} 1.4755; d_4^{20} 1.0029; MR_D 50.97; calc. 50.56.

Found %: N 15.23, 15.34. $C_{10}H_{16}ON_2$. Calculated %: N 15.54.

2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine had not been described in the literature.

B. 2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine. 4.6 g (78%) of 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydrofuran was obtained under the same conditions as in the preceding experiment from 5.9 g (0.032 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 2.51 g (0.032 mole) of ethylenediamine monohydrate after twofold vacuum distillation: m.p. 98-98.2° (6 mm); 101° (8 mm); n_D^{20} 1.4789; d_4^{20} 0.9881; MR_D 59.77; calc. 60.21.

Found %: N 13.58, 13.67. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine had not been described in the literature.

5. Preparation of Imidazoles from the 3,4-Diketones of the Tetrahydrofuran Series*

A. 4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole. A mixture of 0.13 g (0.001 mole) of hexamethylenetetramine and 3 g of ammonium acetate was dissolved in 20 ml of glacial acetic acid and boiled for 1 hour with a reflux condenser. The reaction mixture was then poured out into 100 ml of water and saturated with ammonia while it was being cooled. The solution was repeatedly extracted with ether. After the ethereal extract had been dried with roasted potash and the ether driven off, 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole was isolated.

0.6 g (70.0%) of 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole with a m.p. of 288-289° was obtained after twofold recrystallization from pyridine.

Found %: N 16.79, 17.04. $C_9H_{14}ON_2$. Calculated %: N 16.84.

4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole was soluble in water, alcohol, acetone and hot pyridine. It had not been described in the literature.

B. 2-Phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole. A mixture of 1.6 g (0.01 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4, 1.06 g (0.01 mole) of benzaldehyde and 10 g of ammonium acetate was dissolved in 50 ml of glacial acetic acid and heated for 1 hour with a reflux condenser. The reaction mixture was poured out into 300 ml of water and filtered free of suspension through activated carbon. The transparent solution was saturated with ammonia while being cooled, after which a voluminous precipitate settled out which was dissolved in 10 ml of hot pyridine and precipitated with 10 ml of hot water. 2 g (82%) of 4,4,6,6-tetramethyl-2-phenyltetrahydrofuro-(3,4)-imidazole was obtained after twofold recrystallization from acetone: m.p. 253-254°.

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* The imidazoles were prepared by the method described for the synthesis of imidazoles from benzene [8].

Found %: N 11.46, 11.36. $C_{15}H_{18}ON_2$. Calculated %: N 11.56.

2-Phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole was soluble in hot acetone, alcohol and pyridine and insoluble in water; it had not been described in the literature.

C. 4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole. 4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole was obtained from 1.84 g (0.01 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 0.26 g (0.002 mole) of hexamethylenetetramine under conditions analogous to those for the preparation of 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole: m.p. 193-194° (after twofold recrystallization from dichloroethane). The yield was 1.2 g (80%).

Found %: N 14.62, 14.17. $C_{11}H_{18}ON_2$. Calculated %: N 14.42.

4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole was quite soluble in water, pyridine, acetone, carbon tetrachloride, chloroform and hot dichloroethane. It had not been described in the literature.

SUMMARY

1. The oxidation with selenium dioxide of ketones of the tetrahydrofuran series with tertiary carbon atoms in positions 2 and 5 can serve as a convenient preparative method of obtaining diketones in which carbonyl groups are located in positions 3 and 4. 2,2,5,5-Tetramethyltetrahydrofurandione-3,4 and 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 were prepared in respective yields of 83.5% and 86.5% of the theoretical.

2. The 3,4-diketones of the tetrahydrofuran series appear to be convenient starting materials for the synthesis of condensed heterocyclic systems, the structure of which includes the tetrahydrofuran, and the quinoxaline, dihydropyrazine or imidazole rings.

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DISCUSSION

RESPONSE TO THE ARTICLE OF G. V. TSITSISHVILI APROPOS OF THE WORK OF A. A. KALANDIYA ENTITLED "CALCULATION OF MOLECULAR VOLUMES OF INORGANIC COMPOUNDS OF THE $A_nB_mO_s$ TYPE"

A. A. Kalandiya

An article by G. V. Tsitsishvili [1] has been devoted to the critical analysis of my work [10], "Calculation of Molecular Volumes of Inorganic Compounds of the $A_nB_mO_s$ Type".

Tsitsishvili did everything possible to distort the basic approach of my work and reproaches me because in my article " . . . : He has not taken into consideration Butlerov's theory of chemical structure". However, before having made a statement so inaccurate (as will be shown below), it would have been helpful if Tsitsishvili had stated that in all his works [3-9] on the so-important topic of the structure of compounds, not only was the Butlerov theory of chemical structure never considered, but there was an overall silence concerning the very existence of A. M. Butlerov's structural theory.

On the basis of the substance of the works of Tsitsishvili and also of his recent communication concerning my work [1], one is forced to conclude that Tsitsishvili was trying to create the impression that he is an opponent of the "theory of resonance", thereby distracting attention from his own methodologically defective Machist-idealistic concepts.

It is impossible to describe his expressions except with use of the "terminology of the resonance concept" which he supported at the All-Union Congress on the State of the Theory of Chemical Structure in Organic Chemistry [2].

Not to dwell on the other works of Tsitsishvili based on an idealistic conception of the question, I pass over to the critical review of my article [10]. It was certainly far from my thoughts that Tsitsishvili was incapable of understanding the point of my work in the form in which it was set forth. Tsitsishvili, in his recently published article, disorients the reader by incorrectly interpreting my basic positions.

For example, Tsitsishvili maintains that I had attempted to calculate the forces F_2, while actually I calculate the radius R_{z_1}. As is evident from a mere glance at my work [10], I was undertaking to provide a method for calculating the molecular volumes and not the forces F_2. Apart from this, and contrary to the assertions of Tsitsishvili, in my entire paper, all calculations were subordinated to the goal of determining the molecular volume; this requires the quantities $R_{z_1z_2z_3}$, i.e., the distances between the centers of the cation and anion, and not R_{z_1} as Tsitsishvili incorrectly indicates.

It should be noted that Tsitsishvili endeavors to maintain that I was calculating the influence of some sort of extraneous ions on the distance between the ions B_m^{z+} and O_s^{f-}, concerning which nothing whatever was said in my article.

For clarity I present in its entirety a quotation, containing the essence of Tsitsishvili's criticism of my work. Tsitsishvili writes: "There is practically no basis for the expression for the attractive forces (see Equation 1). The introduction of the constant coefficient $\underline{A}$, which Kalandiya glorifies as the 'Madelung Constant', has no basis here at all. The constant coefficient in the energy of attraction is a function of the type of lattice in the solid; it is usually used for the electrostatic calculation of the lattice energy. Here Kalandiya attempts to calculate the reaction between $\underline{m}$ positive ions B and $\underline{s}$ negative ions O. It is nowhere shown that the attractive force, F_1, is actually proportional to z_3 and z_4. It is appropriate to point out that in the foregoing foggy text, it is almost impossible to comprehend the significance of z_1, z_2, z_3, and z_4. For instance, Kalandiya writes that 'z_1 = the charge employed for the bond with element A.' One must ask – the value of what charge and, probably, employed, rather than occupied by, as the author writes:) * for the bonds of what ions (and not elements, as the author confuses it)?"

In the first place it should be noted that in my work the symbols z_1, z_2, z_3, and z_4 denote the charges of ions and covalent bonds of elements entering into a complex substance. For example: in sodium sulfate the bond between sodium and oxygen is ionic while the bond of sulfur with oxygen is slightly polar and ions are generally not formed via bonding of sulfur with oxygen. Many such examples could be adduced. On this basis and in order to avoid confusion, since this is generally understood, in my work I preferred to call the simple substance an element.

I wish to note the following in order to avoid incorrect interpretations: it is well known that the properties of chemical bonds of both diatomic and polyatomic moledules are identical and there is no basis to employ Coulomb's law for diatomic molecules only. In addition, both in diatomic and in polyatomic molecules each nucleus actually interacts not with point charges but with an electron cloud. The distribution of the density of this electron cloud changes markedly with changes in the distance between nuclei. In spite of this it is conventional to consider that the attractive force of two ions of opposite sign obeys Coulomb's law. This involves the assumption that the charges of the ions are concentrated at one point.

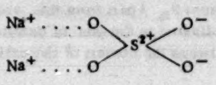
It should be noted here that in crystal lattices of binary compounds, for example, in sodium chloride, we have to do with a high-molecular complex compound $(NaCl)_n$. In spite of this it is well known that the attractive force of such crystalline compounds is calculated in the same way as for the simple binary compound. The energy of a mole of the crystalline substance is also calculated on the assumption that the force of interaction between each pair of ions obeys Coulomb's law, including Madelung's constant and not the Coulomb law of repulsion $\frac{B}{R^n}$.

I assumed in exactly the same way that the force of interaction between each pair of ions obeys Coulomb's law for polyatomic molecules. It was thereby taken into account that compound atoms basically influence each other through intermediate atoms and not directly. On the basis of this and the experimental data, the influence of the cation A_n^+ was taken into account for the attractive force F_1 between each pair of ions $B_mO_s^{f-}$ by means of the values z_3 and z_4; the proportionality of the influence of the cation A_n^+, contrary to the assertion of Tsitsishvili, was demonstrated on the basis of the results of 75 calculations and their comparison with the experimental data.

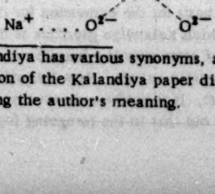
The constant coefficient A (Madelung's constant) introduced by me in the given case can also be considered necessary and justified. It is far from my thoughts, however, that my attempts to arrive at the calculation of the interatomic distances and molecular volumes were ideal and require no further development and precision.

To distract the attention of the reader from his own Machist-idealist errors which he has tolerated from the beginning of his career to the present time, Tsitsishvili maintains that the substance of my article amounts to an anti-Butlerov representation of the polystructure of molecules. However, as even the non-expert reader can readily see, my calculation of the molecular volume demonstrated that there is only one structural formula depicting the structure of the compound for each real compound; the simultaneous existence of other structures is thereby contradicted. Consequently, the results of my work are found to be in agreement with the teachings of A. M. Butlerov.

For example: Na_2SO_4 is either constructed according to the formula, composed of the ions Na^+, S^{2+}, and O^- with four covalent S – O bonds:



or according to the formula consisting of the ions Na^+, S^{6+} and O^{2-}:



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* The Russian word originally used by Kalandiya has various synonyms, and might be translated as: occupied by, busied with, employed for. In the translation of the Kalandiya paper discussed here, Consultants Bureau chose the latter translation as most probably conveying the author's meaning.

Calculating the molecular volume for Na_2SO_4 according to my method [10] for the first structure, we find on the basis of the radii of the "mono-charged" ions that it is equal to 51.1 $Å^3$. It should actually be 53.2 $Å^3$, i.e., the error amounts to only 2.1 $Å^3$.

Assuming that Na_2SO_4 has the second structure, its molecular volume calculated according to my method on the basis of the ionic radii [11], is equal to 24.0 $Å^3$ instead of 53.2 $Å^3$, i.e., in this case the deviation is equal to 29.2 $Å^3$.

Thus, my calculation of the molecular volumes definitely demonstrates the probability of the first structure for Na_2SO_4.

A similar calculation was carried out by me for all the compounds which are set forth in Tables 3, 4, and 5 [10], but only the results obtained for one of the assumed structures for each distinct compound are set forth there. This again demonstrates that I adhere to the position that there is only one structural formula for each real compound which depicts the chemical structure of that compound. Consequently, contrary to the assertion of Tsitsishvili, the substance of my work is based not on a multi-structural, but on a monostructural theory.

As regards the sentence: "It must be assumed that the structure . . . . . in the second variant predominates over all the other structures expressed by the other variants in the state of mutual superposition of one over another."; [10], I recognize it to be erroneous and not proceeding from the results of my work and have so declared at the opportune time.

The attention of the reader should finally be directed to yet one more example of confusion created by Tsitsishvili. He writes: "It is impossible to understand why Kalandiya used K = 1.044 for $NaIO_4$ . . . . . Kalandiya states that he takes the coefficient of repulsion as 9. When he returns to the calculation of the $NaIO_4$ example, he assumes that it 'averages 7' ". Tsitsishvili further writes: "What is the average coefficient of repulsion, and, strictly speaking, on the basis of what data does Kalandiya take it to be 7 for $NaIO_4$, 7.3 for $NaBrO_4$, 8.3 for $CoWO_4$ and 9.3 for $PbMoO_4$?". In my work the number K is the ratio of the interatomic distances to the coordination number. In agreement with existing data [11], with a coordination number of 8 and a degree of repulsion of 7, as occurs in my case, K for $NaIO_4$ = 1.044. As is evident from the table presented on page 1638 of the article [10], inasmuch as $\underline{n} = 7$ for oxygen, the average value of n for $CoWO_4$ is equal to 8.3

However, Tsitsishvili, without altering his method of ignoring entirely plain facts, in place of this quantity, $\underline{n}$, as an index of the order of the radical, calls the attention of the reader to an entirely baseless discussion of this very simple question, substituting for the above-mentioned ratio another symbol $\underline{n}$, found in the denominator, as a constant coefficient equal to 9.

Further, as is well known, in the equation $F = F_1 + F_2$ (3) [10], the right hand side of the equation is subject to partial integration. Avoiding this fact, Tsitsishvili talks of mechanical separation of the energy of interaction from the energy of attraction and repulsion as if it were my invention, saying: "the repulsion force mysteriously arises for Kalandiya at the instant of the mutual approach of the ions" [1]. By this Tsitsishvili assiduously attempts to conceal from the reader that what he calls the "very mysterious" Coulomb force is the action of the forces of attraction and repulsion between charged envelopes of ions (not the Coulomb force of repulsion), briefly designated in my work as

$$\frac{B}{R^n}.$$

I hope that the examples which I have presented will warn the reader against the confusion created by Tsitsishvili.

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DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN THE SOLID AND LIQUID PHASES DURING CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

III. EQUILIBRIUM IN THE SYSTEM $Co(NO_3)_2-Ni(NO_3)_2-H_2O$ AT 20° [1]

G. I. Gorshtein and N. I. Silantyeva

According to the literature data, cobalt nitrate and nickel nitrate crystallize in the form of hexahydrates which have identical structures and close crystal lattice parameters[3].

The solubility of these salts is also almost identical. In view of the closeness of the properties of both salts it could be assumed that they are isomorphic and form solid solutions at all possible component ratios. However, as will be evident from the following, cobalt nitrate and nickel nitrate are actually isodimorphic at 20° and have differing crystalline structures. The elucidation of these structures must be the subject of a special study.

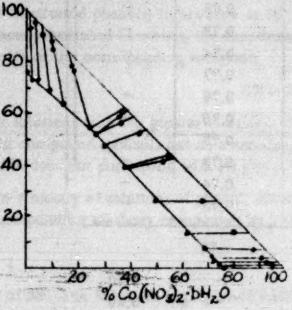

Fig. 1. Equilibrium composition diagram for the system $Ni(NO_3)_2-Co(NO_3)_2-H_2O$ at 20°.

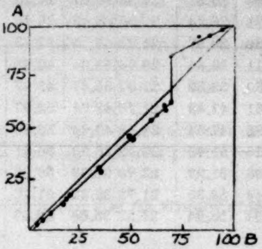

Fig. 2. Phase distribution diagram for the system $Ni(NO_3)_2-Co(NO_3)_2-H_2O$ at 20°. A) % $Ni(NO_3)_2\cdot 6H_2O$ in the solid phase, B) % $Ni(NO_3)_2\cdot 6H_2O$ in the salt component of the mother liquor.

The methods of analysis were analogous to those indicated in the description of the results of the investigations of the system: $CoSO_4\cdot(NH_4)_2SO_4-NiSO_4\cdot(NH_4)_2SO_4-H_2O$ [2].

The experimental results are given in the table, in the equilibrium composition diagram (Fig. 1) and in the diagram of the phase distribution of components (Fig. 2).

As is evident from the curves, two series of solid solutions are formed in the system at 20°: one series with a crystal structure of the cobalt nitrate type, and the other of the nickel nitrate type. Cobalt nitrate and nickel nitrate are thus isodimorphic at 20°. In the last two columns of the table the magnitudes of the equilibrium distribution coefficients of the components for various points of each of the two series of solid solutions are given. The magnitude of the equilibrium distribution coefficient of nickel salt in relation to cobalt salt $D_{(Ni,\ Co)}$ is identical in value over the entire region in which solid solutions of the cobalt nitrate type exist, and on the average is equal to 0.72; a single value for the equilibrium distribution coefficient of cobalt salt relative to nickel salt $D_{(Co,\ Ni)}$ is also obtained for the region in which solid solutions with a nickel nitrate structure exist, and is equal on the average to 0.42.

TABLE

Equilibrium in the System $Co(NO_3)_2-Ni(NO_3)_2-H_2O$ at 20°. [I) % $Co(NO_3)_2 \cdot 6H_2O$; II) % $Ni(NO_3)_2 \cdot 6H_2O$; III) % H_2O]

Expt. No.	Analytical results						Composition of the solid phase		Distribution coefficient		Notes
	for the mother liquor			for the solid phase					$D_{eq.(Ni, Co)}$	$D_{eq.(Co, Ni)}$	
	I	II	III	I	II	III	I	II			
1a	77.07	–	22.93	–	–	–	–	–	–	–	Solid solutions with a cobalt nitrate structure
3a	75.17	0.88	23.95	94.26	0.83	4.91	99.19	0.81	0.69	–	
19a	75.55	0.90	23.55	95.79	0.79	3.42	99.22	0.78	0.71	–	
19b	75.42	0.85	23.73	96.33	0.80	2.87	99.21	0.79	0.71	–	
2a	72.82	2.66	24.52	93.22	2.53	4.25	97.52	2.48	0.68	–	
2b	73.60	2.67	23.73	92.60	2.63	4.77	97.38	2.62	0.72	–	
1a	73.23	3.84	22.93	91.35	4.06	4.59	95.92	4.08	0.82	–	
1b	72.64	4.10	23.26	91.63	3.98	4.39	96.05	3.95	0.73	–	
4a	68.94	8.03	23.03	88.05	7.70	4.25	92.37	7.63	0.71	–	
4b	69.25	8.02	22.73	88.92	7.82	3.26	92.21	7.79	0.78	–	
6a	69.75	8.03	22.22	88.74	7.71	3.55	92.35	7.65	0.72	–	
6b	69.40	8.02	22.58	88.06	7.86	4.08	92.17	7.83	0.73	–	
16a	62.02	13.70	24.28	79.67	13.83	6.50	86.13	13.87	0.73	–	
16b	61.95	13.67	24.38	80.81	14.15	5.04	85.72	14.28	0.75	–	
14a	49.71	26.74	23.55	68.46	26.76	4.78	73.24	26.76	0.68	–	
14b	49.80	25.97	24.23	67.54	27.23	5.23	72.40	27.60	0.73	–	
11a	38.11	38.85	23.04	53.34	42.23	4.43	56.97	43.03	0.74	–	
11b	38.84	39.59	21.57	55.37	43.67	0.96	56.15	43.85	0.77	–	
12a	30.81	47.49	21.70	43.71	52.97	3.32	46.05	53.95	0.76	–	
12b	30.88	47.54	21.58	43.94	52.86	3.20	46.22	53.78	0.75	–	
13a	26.15	51.43	22.42	36.53	56.61	6.86	41.10	58.90	0.73	–	
13b	25.98	51.29	22.73	35.39	58.25	6.36	39.08	60.92	0.79	–	
18a	24.44	53.83	21.73	36.22	61.12	2.66	38.02	61.98	0.74	–	
18b	24.34	53.84	21.82	35.68	60.43	3.89	38.25	61.75	0.73	–	
							Average value of D:		0.72		
10a	24.70	54.32	20.98	17.37	78.14	4.49	15.38	84.62	–	0.40	Solid solutions with a nickel nitrate structure
10b	25.16	53.45	21.39	17.89	77.38	4.73	15.83	84.17	–	0.40	
9a	14.84	63.49	21.67	9.91	87.73	2.36	9.31	90.69	–	0.44	
15a	14.53	63.11	22.36	9.99	84.70	5.31	8.51	91.49	–	0.40	
15b	14.51	62.47	23.02	10.03	86.81	3.16	9.26	90.74	–	0.44	
8a	8.82	69.02	22.16	5.63	90.94	3.43	5.02	94.98	–	0.41	
8b	8.78	69.01	22.21	5.57	90.74	3.69	4.93	95.07	–	0.41	
7a	4.71	73.84	21.45	2.96	95.06	1.98	2.79	97.21	–	0.45	
7b	4.76	73.80	21.44	3.03	94.38	2.59	2.79	97.21	–	0.44	
17a	2.08	73.30	24.62	1.39	93.36	3.25	1.20	98.80	–	0.44	
17b	2.09	72.74	25.17	1.47	92.74	5.79	1.28	98.72	–	0.45	
18a	–	76.21	23.79	–	–	–	Average value of D:			0.42	

SUMMARY

The equilibrium in the system $Co(NO_3)_2-Ni(NO_3)_2-H_2O$ at 20° was studied. It was found that at this temperature the components are isodimorphic, and that two series of solid solutions are formed in the system. It was established that the systems are ideal in each of the two regions of existence of a solid solution with a definite strucutre.

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* See Consultants Bureau Translation, page 1355.

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THE HYDROGEN BOND AND THE VISCOSITY OF SOLUTIONS

A. E. Lutsky

The formation of complexes due to hydrogen bonds between alcohol, phenol and acid molecules causes a sharp increase in the viscosity of liquids [1]. Inasmuch as the indicated complexes of molecules of dissolved substances survive in such solvents as benzene, an anomalously increased viscosity of benzene solutions of the substances under consideration is to be expected. Since the viscosity of liquids is determined not only by the coupling forces between molecules (including the hydrogen bond), but also by the mass of the molecules and the number of them in a unit volume, to detect the influence of the coupling forces it is reasonable to compare the values of the viscosity of solutions of identical-by-weight samples of the substances in a given volume of solution. In such solutions the increase in the mass of the molecules of the dissolved substance is accompanied by decrease in the number of molecules in a unit volume, and the difference in viscosity evoked by differences in the mass of the molecules is compensated for to a considerable extent by the differences in the number of molecules of the dissolved substance in a unit volume.

The results of viscosity measurements of the indicated type of solutions of 22 compounds (phenol, its derivatives and substituted phenols) in benzene at 50° are set forth in Table 1. As follows from the data obtained in the case of monosubstituted benzenes, the functional groups arrange themselves in a series according to the value of the viscosity of the corresponding solutions:

$$OH > NO_2 > COCH_3 > OCH_3 > CH_3,$$

i.e., form solutions with the greater viscosity, the greater their group moment. Only a solution of the hydroxyl-containing compound (phenol) has an anomalously high viscosity and the OH group occupies a position in the series which does not correspond with its group moment.

The viscosity of solutions of phenol, cresols, m- and p-nitrophenols is greater than the viscosity of solutions of the corresponding methoxy compounds by $7-28 \cdot 10^{-5}$ poise.

TABLE 1

Viscosity of Benzene Solutions (Samples of 0.9984 - 0.9990 g in Approximately 25 ml of Solution) at 50° ± 0.1

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions		
		$\eta_{m-} - \eta_{o-}$	$\eta_{p-} - \eta_{o-}$	$\eta_{OCH_3} - \eta_{OH}$
Nitrobenzene	443			
Nitrophenol: o-	443			
m-	455	+12		
p-	458		+15	
Nitroanisole: o-	454			+11
m-	448	−6		−7
p-	449		−5	−9
Acetophenone	442			
Hydroxyacetophenone: o-	453			
p-	482		+29	
Methoxyacetophenone: o-	456			+3
m-	454	−2		
p-	454		−2	−28
Toluene	436			
Cresol: o-	462			
m-	458	−4		
p-	464		+2	
Cresyl methyl ether: o-	447			−15
m-	444	−3		−14
p-	445		−2	−19
Phenol	449			−9
Anisole	440			

Compounds with a hydrogen bond within the molecule (o-nitrophenol and o-hydroxyacetophenone) differ from the m- and p-isomers which are associated intermolecularly in solution. Thus, their methyl ethers yield solutions with a viscosity not lower but higher than that of solutions of the initial hydroxy compounds. While solutions of o-, m- and p-isomers ordinarily have almost the same viscosity, solutions of o-isomers with intramolecular hydrogen bonds within them have an appreciably smaller viscosity (of the order of 15-29 · 10^{-5} poise) than their m- and p-isomers.

It is characteristic that all the relationships noted for benzene solutions are observed in the case of alcoholic solutions of the indicated substances.

In Table 2 are set forth the results of viscosity measurements of alcoholic solutions of 37 compounds of the indicated type (phenol, benzoic acid and their substituted and derived compounds). The functional groups (except OH and COOH) also arrange themselves by value of the viscosity of solutions of monosubstituted benzenes in alcohol in a series which basically agrees in order with that of their group moment:

$$COOH > OH \approx COCH_3 > NO_2 > CHO > COOC_2H_5 > OCH_3 > CH_3.$$

In alcohol phenol and particularly benzoic acid also yield solutions with an anomalously high viscosity related to the influence of intermolecular association. The viscosity of a solution of m- and p-hydroxyacetophenones is greater than the viscosity of a solution of the metameric m- and p-methoxybenzaldehydes by 3-5%. Alcoholic solutions of methoxy compounds, like benzene solutions, have an appreciably smaller viscosity than their initial hydroxy compounds. Solutions of esters of the acids (benzoic and hydroxybenzoic) also have a sharply reduced viscosity in comparison with that of solutions of the acids themselves.

TABLE 2

Viscosity of Alcoholic Solutions (Samples of 0.9984-0.9990 g in Approximately 25 ml of Solution) at 50° ± 0.1

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions			
		$\eta_{m-} - \eta_{o-}$	$\eta_{p-} - \eta_{o-}$	$\eta_{OCH_3} - \eta_{OH}$	$\eta_{COOC_2H_5} - \eta_{COOH}$
Nitrobenzene	721				
Nitrophenol: o-	698				
m-	724	+26			
p-	728		+30		
Nitroanisole: o-	717			+19	
m-	716	−1		− 8	
p-	722		+5	− 6	
Acetophenone	726				
Hydroxyacetophenone: o-	725				
m-	760	+35			
p-	775		+50		
Methoxyacetophenone: o-	726			+ 1	
m-	731	+ 5		−29	
p-	733		+ 7	−42	
Benzaldehyde	718				
Hydroxybenzaldehyde: o-	729				
m-	765	+36			
Methoxybenzaldehyde: o-	733			+ 4	
m-	737	+ 4		−28	
p-	737	+ 4			
Ethyl hydroxybenzoate: o-	708		+4		−28
m-	751	+43			−46
p-	751		+43		−63
Toluene	682				
Cresol: o-	738				
m-	741	+ 3			
p-	743		+ 5		
Cresyl methyl ethers: o-	704			−34	
m-	701	− 3		−40	
p-	702		− 1	−41	
Phenol	726				
Anisole	693			−33	
Benzoic acid	734				
Hydroxybenzoic acid: o-	736				
m-	797	+61			
p-	814		+78		
Ethyl benzoate	711				−23

Compounds with an intramolecular hydrogen bond, in contrast to their intermolecularly associated m- and p-isomers, yield solutions with a viscosity even lower than that of their methyl ethers and their non-associated metamers (o-hydroxyacetophenone and o-methoxybenzaldehyde) in spite of the presence of the hydroxyl group. In alcohol o-hydroxyacetophenone, o-nitrophenol, o-hydroxybenzoic acid, o-hydroxybenzaldehyde and ethyl o-hydroxybenzoate also tend to form an intramolecular hydrogen bond and to yield solutions which have an appreciably lower viscosity than that of their m- and p-isomers. All these correlations between the properties of the isomers are absent in the cresols, the o-isomer of which does not form an intramolecular hydrogen bond.

Thus, the same relations for the viscosities of alcohol solutions of non-associated and associated inter- and intramolecular compounds are found as for benzene solutions. Judging by certain data [2], such a relation also exists for the viscosity of 0.01 N solutions in amyl acetate; evidently in alcoholic solutions of the concentration under consideration the tendency of molecules of the dissolved substance, at least in part, toward the formation both of intramolecular hydrogen bonds and toward the formation of complexes between molecules due to the hydrogen bond is maintained. Data for the density of solutions [3] also leads to similar conclusions.

The correlations for the viscosity of solutions established above are identical with those detected for the viscosity of individual substances in the liquid state. This permits an estimate to be made from the data for the viscosity of solutions of corresponding compounds concerning the presence and character of association of a dissolved substance; this is particularly important for compounds which decompose on fusion.

EXPERIMENTAL

The synthesis and purification of the substances which were studied was carried out in accordance with the literature data. The purification of the solvents was described in the preceding article [3]. The relative viscosity was measured in an Ostwald viscosimeter. The viscosimeter was calibrated with the corresponding pure solvent. The measurement was carried out in a viscosimeter with the time of outflow for benzene equal to 279.9 seconds; for cresol solutions a viscosimeter was used with a time of outflow for benzene of 67.2 seconds. In the determination of the viscosity of alcoholic solutions the time of outflow of pure alcohol amounted to 120.0 and 129.2 seconds. In the calculations $\eta \cdot 10^5$ at 50° and the density were taken as 436 and 0.8464 for benzene, and as 702 and 0.7778 for alcohol. The value of the density of the solutions, necessary for the calculation of the value of η [3] was simultaneously determined. The data set forth in the tables for the viscosity of the solutions are the averages of several experiments which deviated from each other by not more than 0.4%.

SUMMARY

1. The values for the viscosity of solutions at 50° in benzene and in ethyl alcohol were determined for a number of phenols and acids and their esters.

2. It was established that the same relationships of the viscosities of non-associated and associated inter- and intramolecular compounds apply to benzene and alcohol solutions as to the individual substances in the liquid state.

3. The data for the viscosity of solutions of corresponding compounds can be utilized for the qualitative determination of the presence and character of association of a dissolved substance.

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* See Consultants Bureau Translation, page 73.

Compounds with an intramolecular hydrogen bond[1] [illegible] isomers and [illegible] yield solutions with a viscosity even lower than that of their [illegible] and [illegible] [illegible] hydroxy [illegible] o-nitrophenol [illegible] which form an intramolecular hydrogen bond and [illegible] which have an appreciably lower viscosity than that of their m- and p-isomers. All these [illegible] in the [illegible], the o-isomer of which does not form an intramolecular hydrogen bond.

Thus, the same relations for the viscosities of alcohol solutions [illegible] intramolecular compounds are found as for benzene solutions. [illegible] for the viscosity of 0.07 N solutions in ethyl acetate [illegible] of the dissolved molecules [illegible] hydrogen bonds and [illegible] the formation of [illegible] maintained. Data for the density of solutions [3] also leads to similar conclusions.

The correlations for the viscosity of solutions established above are identical with those obtained for the viscosity of individual substances in the liquid state. This permits us to [illegible] from the data for the viscosity of solutions of compounds [illegible] concerning the presence and [illegible] of association of a substance; this is particularly important for compounds which decompose on fusion.

EXPERIMENTAL

The synthesis and purification of the substances which were studied were carried out in accordance with the literature data. The purification of the solvents was described in the preceding communication [4]. The relative viscosity was measured in an Ostwald viscosimeter. The viscosimeter was calibrated with [illegible] pure toluene. The measurement was carried out in a viscosimeter with the time of outflow of benzene [illegible] seconds; for alcohol solutions a viscosimeter was used with a time of outflow for [illegible] of [illegible] seconds. [illegible] the viscosity of alcohol [illegible] the time of outflow of pure alcohol [illegible] seconds. In the calculations [illegible] and the density were taken as [illegible] for benzene and [illegible] for alcohol. The value of the density of the solutions, necessary for the calculation of the viscosity [illegible], was simultaneously determined. The data set forth in the tables for the viscosity of the solutions are the averages of several experiments which deviated from each other by not more than 0.4%.

SUMMARY

1. The values for the viscosity of solutions at 20° in benzene and in ethyl alcohol were determined for a number of phenols and acids and their ethers.

2. It was established that the same relationships of the viscosities of [illegible] associated and unassociated [illegible] and intramolecular compounds apply to benzene and alcohol solutions [illegible].

3. The data for the viscosity of solutions of corresponding compounds can be utilized for the qualitative determination of the presence and character of association of substances.

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* See Consultants Bureau Translation, page [illegible].

THE REACTION OF NITRATES OF METALS OF THE FIRST GROUP OF THE D. I. MENDELEEV PERIODIC TABLE WITH CADMIUM NITRATE IN MELTS

I. CONDUCTANCE OF THE BINARY SYSTEMS: LITHIUM NITRATE–CADMIUM NITRATE AND SODIUM NITRATE–CADMIUM NITRATE IN MELTS

N. P. Popovskaya and P. I. Protsenko

The chemistry of nitrates in melts has been relatively little investigated. At the same time the study of the character of the reaction of nitrates in the fused state is of practical and theoretical interest.

Experimental material on the specific conductance and numerical values of the absolute and relative temperature coefficients for the two binary systems: $LiNO_3-Cd(NO_3)_2$ and $NaNO_3-Cd(NO_3)_2$, the phase equilibrium diagrams of which, obtained by a visual-polytherm method of physico-chemical analysis, have already been described [1, 2], is presented in the present communication.

According to the literature data known to us, a total of only four binary nitrate systems have been studied in melts by the conductance method, which was evidently inadequate, since many authors [3, 4, 5] have repeatedly returned to certain of these indicated systems.

EXPERIMENTAL

The lithium nitrate–cadmium nitrate and sodium nitrate–cadmium nitrate systems described below were first investigated by the conductance method. The measurement of specific conductance was carried out in an apparatus assembled according to Kohlrausch with the substantial modifications described in the works of Belyaev and Mironov [6, 7].

The vessel for measuring the electrical conductance was calibrated with twice recrystallized, chemically pure, fused potassium nitrate. The numerical value for the conductance of potassium nitrate at various temperatures, which was necessary for determining the capacity of the vessel, was taken from Jaeger and Kapma [8]. The precision of the specific conductance measurements of the pure components was controled by comparison of our data with the data of the above-named investigators.

The specific conductance was measured polythermally through a range of 5-8° and was calculated from the well-known formula: $\kappa = \frac{C}{R}$. Isotherms were constructed for the polytherms through a range of 20°. The values of the absolute and relative temperature coefficients were calculated for the isotherms obtained, respectively, from the formulas:

$$\alpha = \frac{\kappa_2 - \kappa_1}{t_2 - t_1} \quad \text{and} \quad \beta = \frac{\kappa_2 - \kappa_1}{t_2 - t_1} \cdot \frac{1}{\kappa_{av.}} .$$

Binary System Cadmium Nitrate–Lithium Nitrate. The phase equilibrium diagram of the indicated system (state–temperature) has previously been described by one of us [1]. It consists of a simple eutectic. From the specific conductance measurements of the salt mixtures of the named components 19 polytherms were obtained, from the data of which seven isotherms were constructed: 200, 220, 240, 260, 280, 300, 320° (Fig. 1, Table 1). The system could not be investigated for compositions containing less than 15 equimolecular percent of cadmium nitrate. With lesser contents of the latter, decomposition of the melt is observed, accompanied by evolution of nitrogen dioxide.

Binary System Cadmium Nitrate–Sodium Nitrate. The composition–temperature equilibrium phase diagram of this system has been described previously [2] and also consists of a simple eutectic. The specific conductance of the binary mixtures was investigated in the temperature range of from 160 to 320°, and 19 polytherms were graphically drawn; by choosing points from these, 8 isotherms were constructed for the following temperatures: 180, 200, 220, 240, 260, 280, 300, 320° (Fig. 2, Table 2).

TABLE 1

Specific Conductance of Salt Mixtures in the System $LiNO_3-Cd(NO_3)_2$

Expt. No.	$LiNO_3$ (in equimolecular %)	Specific conductance κ at a temperature (in °) of							$\alpha\cdot10^{-3}$	$\beta\cdot10^{-3}$	$\alpha\cdot10^{-3}$	$\beta\cdot10^{-3}$
		200	220	240	260	280	300	320	220-260°	260-300°	220-260°	260-300°
1	30	–	–	–	–	–	0.206	0.278	–	–	–	–
2	35	–	–	–	–	–	0.242	0.311	–	–	–	–
3	37.5	–	–	–	0.152	0.200	0.262	0.334	–	–	2.75	13.48
4	40.0	–	–	–	0.164	0.219	0.286	0.360	–	–	3.05	13.68
5	42.5	–	–	0.129	0.180	0.240	0.308	0.381	–	–	3.2	13.17
6	45.0	–	0.092	0.138	0.190	0.252	0.319	0.392	2.45	17.5	3.6	12.60
7	46.5	0.066	0.108	0.157	0.214	0.278	0.345	0.418	2.65	16.6	3.8	11.70
8	48.0	0.071	0.114	0.165	0.223	0.288	0.357	0.430	2.72	16.7	3.35	11.60
9	50	0.082	0.129	0.184	0.241	0.306	0.372	0.447	2.8	15.16	3.27	10.68
10	52.5	0.101	0.151	0.208	0.268	0.334	0.405	0.483	2.93	14.01	3.43	10.19
11	55	–	0.162	0.222	0.287	0.358	0.434	0.511	3.12	13.94	3.67	10.00
12	57.5	–	0.185	0.246	0.314	0.390	0.465	0.546	3.22	12.97	3.77	9.68
13	60.0	–	0.200	0.264	0.336	0.400	0.490	0.569	3.4	12.76	3.85	9.30
14	65	–	–	0.285	0.361	0.440	0.517	0.600	–	–	3.9	8.88
15	70	–	–	0.318	0.394	0.476	0.562	0.650	–	–	4.2	8.70
16	75	–	–	0.370	0.452	0.535	0.620	0.706	–	–	4.8	7.80
17	80	–	–	–	0.470	0.575	0.680	0.765	–	–	5.25	9.10
18	90	–	–	–	0.567	0.690	0.810	0.925	–	–	6.07	7.50
19	100	–	–	–	0.795	0.930	1.070	1.210				

TABLE 2

Specific Conductance of Salt Mixtures in the System $NaNO_3-Cd(NO_3)_2$

Expt. No.	$NaNO_3$ (in equimolecular %)	Specific conductance κ at a temperature (in °) of								$\alpha\cdot10^{-3}$	$\beta\cdot10^{-3}$	$\alpha\cdot10^{-3}$	$\beta\cdot10^{-3}$
		180	200	220	240	260	280	300	320	220-260°	260-300°	220-260°	260-300°
1	25	–	–	–	–	0.105	0.1495	0.195	0.245	–	–	2.25	15.07
2	30	–	0.032	0.056	0.088	0.132	0.1795	0.230	0.279	1.9	20.65	2.45	13.55
3	32.5	0.021	0.042	0.073	0.115	0.154	0.205	0.257	0.307	2.02	17.90	2.57	12.52
4	34	0.025	0.047	0.083	0.120	0.167	0.218	0.269	0.319	2.12	17.20	2.55	11.70
5	36	0.028	0.055	0.093	0.132	0.180	0.230	0.284	0.335	2.18	16.15	2.60	11.20
6	37.5	0.031	0.058	0.097	0.141	0.187	0.240	0.292	0.346	2.25	15.90	2.62	10.90
7	40	0.043	0.073	0.115	0.158	0.208	0.263	0.315	0.369	2.30	14.40	2.68	10.19
8	42.5	0.045	0.080	0.125	0.176	0.227	0.283	0.336	0.390	2.57	14.60	2.70	9.66
9	45	0.055	0.090	0.136	0.190	0.243	0.302	0.360	0.416	2.70	14.24	2.90	9.59
10	47.5	0.061	0.096	0.148	0.203	0.259	0.320	0.382	0.446	2.77	13.67	3.10	9.48
11	50	–	0.111	0.160	0.219	0.278	0.343	0.406	0.470	2.98	13.56	3.20	9.33
12	52.5	–	–	0.180	0.243	0.307	0.374	0.442	0.510	3.18	13.03	3.38	9.01
13	55	–	–	–	0.266	0.324	0.389	0.460	–	–	–	3.40	8.69
14	57.5	–	–	–	0.284	0.354	0.424	0.485	0.564	–	–	3.30	7.80
15	60	–	–	–	0.306	0.378	0.449	0.521	0.592	–	–	3.60	7.90
16	65	–	–	–	–	0.408	0.488	0.568	0.646	–	–	4.00	8.19
17	70	–	–	–	–	0.458	0.537	0.614	0.692	–	–	3.90	7.27
18	80	–	–	–	–	–	0.634	0.735	0.792	–	–	–	–
19	100	–	–	–	–	–	–	–	0.920	–	–	–	–

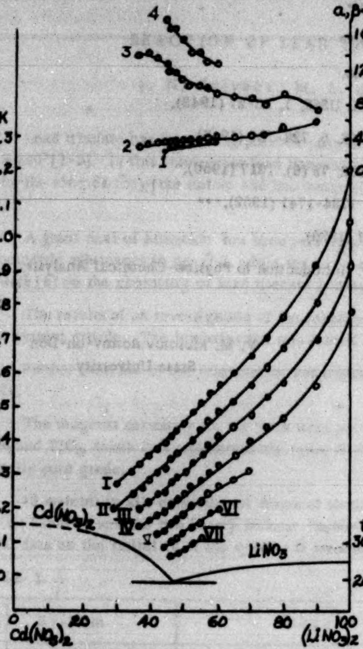

Fig. 1. Specific conductance isotherms and temperature coefficients of the binary system consisting of the nitrates of cadmium and lithium. Temperature coefficients: Absolute: 1) 220-260°; 2) 260-300°; Relative: 3) 260-300°; 4) 220-260°. Isotherms: I) 320°; II) 300°; III) 280°; IV) 260°; V) 240°; VI) 220°; VII) 200°.

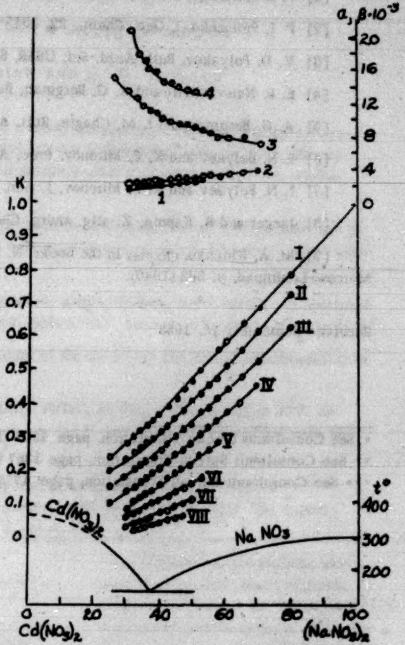

Fig. 2. Isotherms of specific conductance and temperature coefficients of binary systems consisting of the nitrates of cadmium and of sodium. Temperature coefficients: Absolute: 1) 220-260°; 2) 260-300°; Relative: 3) 260-300°; 4) 220-260°. Isotherms: I) 320°; II) 300°; III) 280°; IV) 260°; V) 240°; VI) 220°; VII) 200°; VIII) 180°.

The absence of chemical reaction in the melts between cadmium nitrate on the one hand and lithium nitrate and sodium nitrate on the other hand was established by us from the composition—temperature equilibrium phase diagrams of the systems [1, 2], which was also quite convincingly confirmed by the form of the conductance isotherms and of the absolute and relative temperature coefficient curves. According to M. A. Klochko's classification [9], we have here the "third type" of conductance in binary systems, i.e., a case in which the conductance regularly increases from the more poorly conducting component, cadmium nitrate to the better conducting nitrates of lithium and sodium.

SUMMARY

1. The conductance of binary mixtures consisting of cadmium nitrate—lithium nitrate and cadmium nitrate—sodium nitrate in melts was investigated.

2. It was shown that the conductance isotherms increase almost rectilinearly in the melts from the more poorly conducting cadmium nitrate to the better conducting nitrates of lithium and of sodium.

3. It was confirmed that in melts, lithium nitrate and sodium nitrate do not react chemically with cadmium nitrate.

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* See Consultants Bureau Translation, page 1351 ff.

** See Consultants Bureau Translation, page 1357 ff.

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REACTION OF LEAD TITANATE WITH SALTS IN MELTS

I. N. Belyaev, M. L. Sholokhovich and G. V. Barkova

Lead titanate has interesting piezoelectric properties over a broad temperature range up to temperatures above 500°[1-5]. In this connection lead titanate is of exceptional interest both for the radio ceramics industry and for the elucidation of the nature and treatment of the theory of piezoelectricity in compounds of the $MeXO_3$ type.

A great deal of attention has been paid by physicists to the piezoelectric properties of lead titanate and to piezoelectric substances in general, while too little attention has been paid to this subject by chemists. Thus, only one work [6] on the chemistry of lead titanate is known to us.

The results of an investigation of the reaction of lead titanate with salts of monovalent metals are presented in the present article. The investigation was carried out by a visual-polythermal method of fusibility of up to 1100°.

Further increase of the temperature was impossible on account of the volatility and partial decomposition of $PbTiO_3$.

The reagents necessary for the work were prepared as follows: $PbTiO_3$ by two-fold sintering at 900°, of $PbCO_3$ and TiO_2, taken in a stoichiometric ratio; KVO_3 by fusion of c.p. K_2CO_3 and V_2O_5; the other salts were analytically pure grade.

13 systems in all, consisting of diagonal sections of ternary mutual systems with the participation of $PbTiO_3$ (Table 1) and the two binary systems Na_2MoO_4-PbO and Na_2WO_4-PbO were investigated. The experimental data on the fusibility of the systems is presented in Table 2 and on Fig. 1-4.

TABLE 1

Expt. No.	System	Reaction
1	Na, Pb ‖ SiO_3, TiO_3	$Na_2SiO_3 + PbTiO_3 \longleftarrow Na_2TiO_3 + PbSiO_3$
2	K, Pb ‖ SiO_3, TiO_3	$K_2SiO_3 + PbTiO_3 \longleftarrow K_2TiO_3 + PbSiO_3$
3	K, Pb ‖ F, TiO_3	$K_2F_2 + PbTiO_3 \longleftarrow K_2TiO_3 + PbF_2$
4	Na, Pb ‖ F, TiO_3	$Na_2F_2 + PbTiO_3 \longleftarrow Na_2TiO_3 + PbF_2$
5	K, Pb ‖ VO_3, TiO_3	$K_2(VO_3)_2 + PbTiO_3 \longleftarrow K_2TiO_3 + Pb(VO_3)_2$
6	Na, Pb ‖ VO_3, TiO_3	$Na_2(VO_3)_2 + PbTiO_3 \longleftarrow Na_2TiO_3 + Pb(VO_3)_2$
7	K, Pb ‖ CO_3, TiO_3	$K_2CO_3 + PbTiO_3 \longleftarrow K_2TiO_3 + PbCO_3$
8	Na, Pb ‖ CO_3, TiO_3	$Na_2CO_3 + PbTiO_3 \longleftarrow Na_2TiO_3 + PbCO_3$
9	Na, Pb ‖ MoO_4, TiO_3	$Na_2MoO_4 + PbTiO_3 \longleftarrow Na_2TiO_3 + PbMoO_4$
10	Na, Pb ‖ WO_4, TiO_3	$Na_2WO_4 + PbTiO_3 \longleftarrow Na_2TiO_3 + PbWO_4$
11	K, Pb ‖ MoO_4, TiO_3	$K_2MoO_4 + PbTiO_3 \longleftarrow K_2TiO_3 + PbMoO_4$
12	K, Pb ‖ P_2O_7, TiO_3	$K_4P_2O_7 + (PbTiO_3)_2 \longleftarrow 2K_2TiO_3 + Pb_2P_2O_7$
13	Na, Pb ‖ P_2O_7, TiO_3	$Na_4P_2O_7 + (PbTiO_3)_2 \longleftarrow 2Na_2TiO_3 + Pb_2P_2O_7$

Eleven of the sections which were investigated consist of stable diagonal sections of the corresponding ternary mutual systems. The sections for the fluorides, silicates, molybdates and tungstates of sodium and potassium with lead titanate belong to this class. Lead titanate dissolves rather well in melts of sodium and potassium fluorides and silicates. Thus, the solubility of lead titanate in sodium silicate reaches 50% at 1000°. * In the diagonal section $K_2SiO_3-PbTiO_3$ the lead titanate branch in the interval from 35% $PbTiO_3$ at 706° to 51% $PbTiO_3$ at 726° apparently intersects the field of the chemical compound formed within the reciprocal system. The $PbTiO_3$ branch in the $(NaVO_3)_2-PbTiO_3$ section in the interval under investigation apparently intersects two fields, also of chemical compounds.

Particular interest attaches to the diagonal sections $Na_2F_2-PbTiO_3$, $Na_2MoO_4-PbTiO_3$, $Na_2WO_4-PbTiO_3$. Stratification occurs in these three systems – in all cases lead titanate crystallizes under the region of stratification. On the curve $Na_2F_2-PbTiO_3$ the interval of stratification is from 2 to 20% $PbTiO_3$, on the curve $Na_2MoO_4-PbTiO_3$ from 1.5 to 3.5% $PbTiO_3$ and in the case $Na_2WO_4-PbTiO_3$ the stratification exists only in the interval from 1.25 to 2.25% $PbTiO_3$. In the system $Na_2F_2-PbTiO_3$, where the interval of stratification is rather broad (18%) we can establish that the crystallization of $PbTiO_3$ under the region of stratification does not proceed in the triphasic monotectic process (Fig. 1), characteristic of stable diagonal sections of ternary systems.

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* The percentages are equimolecular throughout.

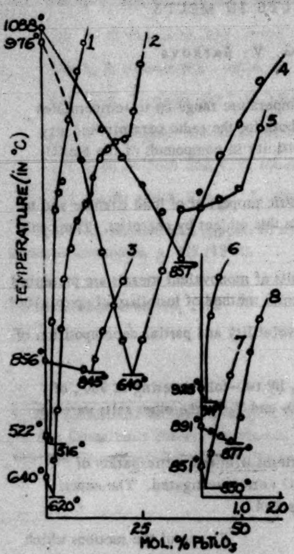

Fig. 1. Fusion curves of stable diagonal sections.
1) $(KVO_3)_2$, 2) $(NaVO_3)_2$, 3) K_2F_2, 4) Na_2SiO_3, 5) K_2SiO_3, 6) K_2MoO_4, 7) Na_2CO_3, 8) K_2CO_3. The second component is $PbTiO_3$.

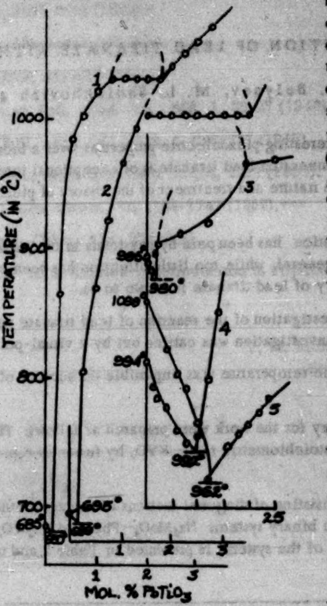

Fig. 2. Fusion curves of diagonal sections.
1) Na_2WO_4, 2) Na_2MoO_4, 3) Na_2F_2, 4) $Na_4P_2O_7$, 5) $K_4P_2O_7$.
The second component is $PbTiO_3$.

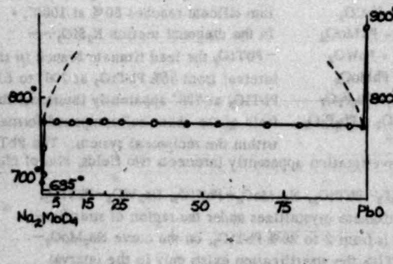

Fig. 3. Fusibility of the binary system Na_2MoO_4-PbO.

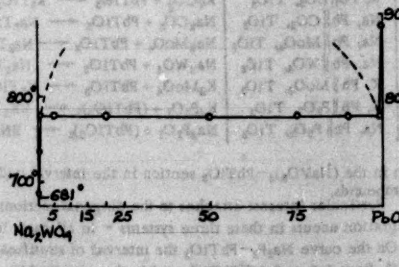

Fig. 4. Fusibility of the binary system Na_2WO_4-PbO.

As has been shown by one of us, the stratification arising in the diagonal sections set forth is the result of the intrusion of two liquid phases with side faces of more complex three dimensional diagrams (prisms, tetrahedra), representing the diagrams of four component systems respectively of six (Na, Pb, Ti ‖ O, F) and four components (Na_2O, PbO, (W)MoO_3, TiO_2).

The tertiary reciprocal systems Na, Pb ‖ WO_4, TiO_3; Na, Pb ‖ F, TiO_3 and Na, Pb ‖ MoO_4, TiO_3, on the stable diagonal sections of which ($Na_2F_2-PbTiO_3$; $Na_2MoO_4-PbTiO_3$; $Na_2WO_4-PbTiO_3$) stratification was detected consisting of the elements (intersecting) of the above-mentioned three-dimensional diagrams of four component systems. The systems Na_2F_2-PbO, Na_2WO_4-PbO, Na_2MoO_4-PbO, investigated in detail by us, (Fig. 3, 4) appear to be the intersecting side faces of these figures. Here stratification exists, occupying almost the entire composition region; the liquid layers of these intersections are displayed on the diagonal sections $Na_2F_2-PbTiO_3$, $Na_2MoO_4-PbTiO_3$, $Na_2WO_4-PbTiO_3$. Thus, of the two liquid phases on the stable diagonal sections of the ternary reciprocal

TABLE 2

Column 1 – % $PbTiO_3$; Column 2 – Temperature at which the first crystals appeared.
(E – Eutectic, P – Intersection of the branches of crystallization)

1	2
$(NaVO_3)_2$—$PbTiO_3$	
0	640
1	620
2	655
3	705
4	787
5	836
7	868
9	895
11	912
13	938
15	957
17	967
19	975
21	977
23	1004
25	1050
E at 620° and 1% $PbTiO_3$	
$K_4P_2O_7$—$(PbTiO_3)_2$	
0	1099
4	1061
6	1043
8	1032
10	1004
12	962
16	988
18	998
20	1005
22	1014
24	1025
P at 962° and 12.5% $PbTiO_3$	
$Na_4P_2O_7$—$(PbTiO_3)_2$	
0	994
1	975
2	964
4	958
6	940
8	930
10	936
12	980
14	1032
P at 922° and 9% $PbTiO_3$	
Na_2WO_4—$PbTiO_3$	
0	685
0.25	865
0.5	985
0.75	1004
1	1022
1.25	1032
1.5	1032
1.75	1032
2	1032
2.25	1032
2.5	1042
2.75	1050
3	1061
3.25	1070
E at 680° and 0.2% $PbTiO_3$	
Na_2F_2—$PbTiO_3$	
0	995
0.25	994
0.5	989
0.75	985
1	982
1.5	980
1.75	997
2	1004
7	1012
12	1021
19	1065
25	1070
E at 980° and 1.5% $PbTiO_3$	
Na_2SiO_3—$PbTiO_3$	
0	1088
15	985
20	957
25	930
30	904
35	857
40	924
45	960
50	991
55	1031
E at 857° and 35% $PbTiO_3$	
K_2SiO_3—$PbTiO_3$	
10	854
15	764
20	675
25	675
30	747
40	806
45	816
50	825
55	886
E at 640° and 22.5% $PbTiO_3$	
Na_2MoO_4—$PbTiO_3$	
0	695
0.25	805
0.5	870
0.75	922
1	967
1.25	995
1.5	1004
1.75	1004
2	1004
2.25	1004
2.5	1004
2.75	1004
3	1004
3.25	1004
3.5	1004
3.75% did not dissolve up to 1100°	
E at 689° and 0.2% $PbTiO_3$	
Na_2MoO_4—PbO	
0% PbO	695
0.25	704
0.5	737
From 0.75% to 99.75%	769°
100	886
E at 685° and 0.2% PbO	
Na_2WO_4—PbO	
0% PbO	685
0.25	737
From 0.5 to 99.75%	778°
100	886
E at 681° and 0.1% PbO	
$(KVO_3)_2$—$PbTiO_3$	
0	522
1	516
2	634
3	744
4	762
5	773
7	836
9	884
11	912
E at 516° and 1% $PbTiO_3$	
K_2MoO_4—$PbTiO_3$	
0	928
0.25	1000
0.5	1040
E at 914° and 0.12% $PbTiO_3$	
K_2F_2—$PbTiO_3$	
0	856
10	847
13	897
15	885
18	911
20	935
E at 845° and 12% $PbTiO_3$	
K_2CO_3—$PbTiO_3$	
0	891
0.25	884
0.5	880
0.75	877
1	900
1.25	965
1.5	998
E at 877° and 0.75% $PbTiO_3$	
Na_2CO_3—$PbTiO_3$	
0	851
0.25	865
0.5	912
0.75	942
E at 830° and 0.15% $PbTiO_3$	

systems under consideration, only one consists of components of a stable pair of salts ($Na_2F_2-PbTiO_3$, $Na_2MoO_4-PbTiO_3$, $Na_2WO_4-PbTiO_3$); the other phase consists of PbO obtained by decomposition of $PbTiO_3$ under the influence of NaF, Na_2WO_4, Na_2MoO_4. Both phases were enriched by the decomposition product $PbTiO_3-TiO_3$.

The experimental material set forth confirms the correctness of the views propounded concerning the nature of stratification in ternary reciprocal systems.

It follows from the data obtained that lead titanate, in the character of its reaction with various salts, has much in common with barium titanate [7], and differs from barium titanate only in a considerably better solubility in fused salts, which is probably associated with the lower melting point of $PbTiO_3$ due to the greater polarizability and polarizing action of the Pb^{++} ion in comparison with the Ba^{++} ion.

SUMMARY

1. The fusion diagrams of lead titanate with the fluorides, silicates, pyrophosphates, molybdates, tungstates and carbonates of sodium and potassium were investigated up to 1100°.

2. It was established that lead titanate forms eutectic systems with melts of the fluorides, silicates, carbonates, molybdates, tungstates of sodium and potassium. The eutectic systems can be utilized for cultivating monocrystals of lead titanate from the fused media.

3. A great analogy in chemical properties of lead titanate and barium titanate was established.

4. The fusion diagrams of Na_2WO_4-PbO and Na_2MoO_4-PbO were investigated.

5. It was confirmed that stratification in the stable diagonal sections $Na_2F_2-PbTiO_3$, $Na_2WO_4-PbTiO_3$, $Na_2MoO_4-PbTiO_3$ arises due to the intrusion of two liquid phases with side faces of three-dimensional diagrams of four component systems.

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* See Consultants Bureau Translation, page 469.

BEHAVIOR OF MAGNESIUM IN ALKALINE SOLUTIONS

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The position of magnesium in the electrochemical potential series is due to its considerable chemical activity in aqueous solutions of electrolytes. Passivity of magnesium can be observed only in alkaline solutions as well as in solutions of fluorides and chromates. Those solutions are used in technology to create coatings which protect magnesium and its alloys from corrosion.

The capacity of magnesium to become passive in alkaline solutions was noted for the first time by Kistyakovsky [1]. The behavior of magnesium in alkaline solutions was apparently not studied in greater detail. Shilov and Shatunovskaya [2] observed the behavior of magnesium in distilled water at temperatures of 25 and 40°. Under these conditions the rate of reaction between magnesium and water falls with time, while the formation of a protective film is observed on the surface of the metal.

The formation conditions of protective films on magnesium in alkaline solutions at raised temperatures were studied in the present work.

EXPERIMENTAL

Pure magnesium (99.96%) was used for the experiments. The experiments were carried out with cylindrically shaped samples. The surface of a single sample was equal to 30 cm^2.

The acidification of magnesium in alkaline solutions both at room temperature and at raised temperatures was accompanied by vigorous evolution of hydrogen, particularly in the initial stage of the process. The gas evolution considerably decreased with the passage of time. At the same time a compact protective film, having various interference colors depending on its thickness, was formed on the metal.

The question of the chemical nature of the protective films formed on magnesium in alkaline solutions had not been resolved until very recently. Electronographic study indicated that it consists of a hydrate of magnesium oxide having a simple hexagonal lattice in which $\underline{a} = 3.13\ \underline{A}$ and $\underline{c} = 4.75\ \underline{A}$. The electronograms were taken by reflecting beams from the surface of samples covered with the oxide film. It should be indicated that on heating in air a film of magnesium oxide forms on magnesium which has a cubic structure of the sodium chloride type with a lattice constant $\underline{a} = 4.20\ \underline{A}$.

The kinetics of the growth of the protective film was studied under various operating conditions. To this end the weight of the films was determined at various stages of their growth by means of eliminating the films from the metal samples in a 20% solution of chromic anhydride; this dissolves the magnesium oxide and is practically without action on the metal. The samples were kept in the chromic anhydride solution for 30 seconds at room temperature In the course of this time the change in the weight of the sample as a consequence of the solution of the metal itself amounted to 0.3 - 0.5 mg. With a film weight of 5 - 10 mg the error in the determination did not exceed 10%. The reproducibility of the experiments was of the same order of magnitude. The thickness of the film could be evaluated from its weight, taking its specific gravity as equal to the specific gravity of brucite ($\gamma = 2.40$) [3]. The total quantity of oxidized metal was also determined, excluding the weight of the films, as the difference between the weight of the samples of the metal before oxidation and after elimination of the films.

The corresponding weights of the films and the quantity of oxidized metal (in milligrams) depending on the time during which the alkaline solution acted on the metal are set forth in Figs. 1 and 2. The solution contained 810 g/ liter of sodium hydroxide. The experiments were conducted at various temperatures from 20° to the temperature at which the solution boiled (135°). On the right hand side of the ordinate in Fig. 1 are placed the values of the thickness of the films (in microns).

Comparable data for the solution containing 1065 g/liter of sodium hydroxide are set forth in Figs. 3 and 4. In this case formation of a loose precipitate of magnesium oxide hydrate located on top of the compact film was observed at a temperature of 145°.

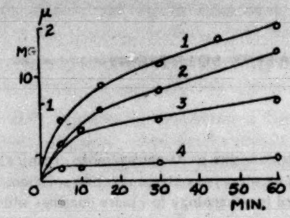

Fig. 1. Growth of the protective film on magnesium at various temperatures. The solution contained 810 g/liter of sodium hydroxide. 1) 135°; 2) 120°; 3) 105°; 4) 20°.

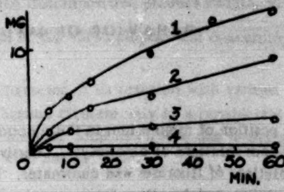

Fig 2. Quantity of metal oxidized as a function of the temperature of the solution. The solution contained 810 g/liter of sodium hydroxide. 1) 135°; 2) 120°; 3) 105°; 4) 20°.

Thus, by raising the temperature of the alkaline solution, the weight of the film and the quantity of metal oxidized was considerably increased. The formation of a protective film inhibits the chemical reaction between metal and solution, which initially occurred rather vigorously. The curves which characterize the change in the quantity of metal oxidized as a function of the time are close to parabolas.

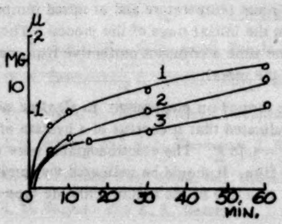

Fig. 3. Growth of the protective film on magnesium at various temperatures. The solution contained 1065 g/liter of sodium hydroxide. 1) 145°; 2) 120°; 3) 105°.

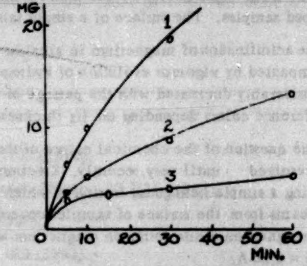

Fig. 4. Quantity of metal oxidized as a function of the temperature of the solution. The solution contained 1065 g/liter of sodium hydroxide. 1) 145°; 2) 120°; 3) 105°.

Since the composition of the film is known, the weight of metal in it can be calculated. The calculations show that a considerable quantity of metal goes over into solution in the process of growth of the protective film. This is illustrated by the data of Fig. 5.

Changing the rate of stirring the solution from 30 to 100 revolutions per minute did not substantially influence the kinetics of the growth of the film. The weight of the film which was formed was also not dependent on the introduction of oxidant into the alkaline solution.

At all stages of the growth of the film of magnesium oxide hydrate, it evidently remained permeable to water and alkaline solutions. The rate of the oxidation of the metal is regulated by diffusion phenomena and depends on the thickness of the protective film being formed. To a considerable extent it depends on the temperature of the solution, and to a lesser degree on the concentration of alkali. During simultaneous increase in the concentration of alkali and of the temperature of the solution, the quantity of metal oxidized appreciably increases, and loosening of the oxide film being formed is observed. This is probably associated with intensification of peptization of magnesium oxide hydrate.

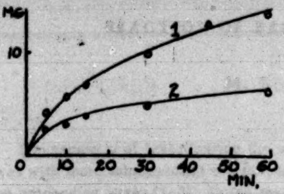

Fig. 5. Oxidation of magnesium in a solution containing 810 g/liter of sodium hydroxide at a temperature of 135°. 1) Total quantity of metal oxidized; 2) quantity of metal in the surface film of magnesium oxide hydrate.

SUMMARY

1. Compact protective films consisting of magnesium oxide hydrate are formed on magnesium in concentrated alkaline solutions at increased temperatures.

2. The process of film growth is self limiting. The rate of growth considerably increases with increased temperature of the solution, and to a lesser degree increases with increasing concentration of alkali.

3. The experiments carried out make it possible to establish the conditions for obtaining films with maximum protective capacity. Compact films with a thickness of about 2 μ can be obtained by treating magnesium with solutions containing 700-800 g/liter of sodium hydroxide at the boiling temperature (130-135°). Protective films on magnesium and its alloys consisting of magnesium hydroxide are of interest from a practical point of view.

In conclusion, I consider it my duty to express my gratitude to Professor A. G. Samartsev for his long-standing interest in the present work.

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REACTION OF BARIUM TITANATE WITH SALTS IN MELTS

M. L. Sholokhovich and I. N. Belyaev

The necessity of investigating the reaction of barium titanate dissolved in melts consisting of various substances with those substances, in relation to its exceptionally interesting piezoelectric properties has been noted in the preceeding works [1-3]. In the present article, the results of investigations of the reaction of barium titanate with fluorides, silicates, carbonates, pyro- and metaphosphates, metaborates, chlorides, molybdates, tungstates and other salts of the alkaline, and of certain divalent, metals in the fused state are set forth. The investigation was carried out up to a temperature of 1200° by a visual-polythermal method.

The salts necessary for the present investigation were prepared as follows: $BaTiO_3$ by two-fold sintering at 1200° of a mixture of $BaCO_3$ and TiO_2 in a stoichiometric ratio; KVO_3, $Pb(PO_3)_2$, $Pb_3(PO_4)_2$ and $Pb(BO_2)_2$ via fusion of chemically pure K_2CO_3 and V_2O_5, PbO and $NH_4H_2PO_4$, PbO and B_2O_3, taken in stoichiometric ratios; $NaPO_3$, KPO_3 and $K_4P_2O_7$ by roasting chemically pure NaH_2PO_4, KH_2PO_4 and K_2HPO_4. The other salts used were chemically pure or analytically pure grade, preliminarily recrystallized.

TABLE 1

Expt. No.	System	Reaction
1	Na, Ba $\|$ F, TiO_3	$2NaF + BaTiO_3 \leftarrow Na_2TiO_3 + BaF_2$
2	K, Ba $\|$ F, TiO_3	$2KF + BaTiO_3 \leftarrow K_2TiO_3 + BaF_2$
3	Li, Ba $\|$ F, TiO_3	$2LiF + BaTiO_3 \leftarrow Li_2TiO_3 + BaF_2$
4	Na, Ba $\|$ Cl, TiO_3	$2NaCl + BaTiO_3 \leftarrow Na_2TiO_3 + BaCl_2$
5	K, Ba $\|$ Cl, TiO_3	$2KCl + BaTiO_3 \leftarrow K_2TiO_3 + BaCl_2$
6	Li, Ba $\|$ Cl, TiO_3	$2LiCl + BaTiO_3 \leftarrow Li_2TiO_3 + BaCl_2$
7	Na, Ba $\|$ SO_4, TiO_3	$Na_2SO_4 + BaTiO_3 \leftarrow Na_2TiO_3 + BaSO_4$
8	K, Ba $\|$ SO_4, TiO_3	$K_2SO_4 + BaTiO_3 \leftarrow K_2TiO_3 + BaSO_4$
9	Li, Ba $\|$ SO_4, TiO_3	$Li_2SO_4 + BaTiO_3 \leftarrow Li_2TiO_3 + BaSO_4$
10	Na, Ba $\|$ MoO_4, TiO_3	$Na_2MoO_4 + BaTiO_3 \leftarrow Na_2TiO_3 + BaMoO_4$
11	K, Ba $\|$ MoO_4, TiO_3	$K_2MoO_4 + BaTiO_3 \leftarrow K_2TiO_3 + BaMoO_4$
12	Na, Ba $\|$ WO_4, TiO_3	$Na_2WO_4 + BaTiO_3 \leftarrow Na_2TiO_3 + BaWO_4$
13	Na, Ba $\|$ PO_3, TiO_3	$2NaPO_3 + BaTiO_3 \leftarrow Na_2TiO_3 + Ba(PO_3)_2$
14	K, Ba $\|$ PO_3, TiO_3	$2KPO_3 + BaTiO_3 \leftarrow K_2TiO_3 + Ba(PO_3)_2$
15	Pb, Ba $\|$ PO_3, TiO_3	$Pb(PO_3)_2 + BaTiO_3 \leftarrow PbTiO_3 + Ba(PO_3)_2$
16	Pb, Ba $\|$ PO_4, TiO_3	$Pb_3(PO_4)_2 + 3BaTiO_3 \leftarrow 3PbTiO_3 + Ba_3(PO_4)_2$
17	Na, Ba $\|$ P_2O_7, TiO_3	$Na_4P_2O_7 + 2BaTiO_3 \leftarrow 2Na_2TiO_3 + Ba_2P_2O_7$
18	K, Ba $\|$ P_2O_7, TiO_3	$K_4P_2O_7 + 2BaTiO_3 \leftarrow 2K_2TiO_3 + Ba_2P_2O_7$
19	Na, Ba $\|$ VO_3, TiO_3	$2NaVO_3 + BaTiO_3 \leftarrow Na_2TiO_3 + Ba(VO_3)_2$
20	K, Ba $\|$ VO_3, TiO_3	$2KVO_3 + BaTiO_3 \leftarrow K_2TiO_3 + Ba(VO_3)_2$
21	Na, Ba $\|$ SiO_3, TiO_3	$Na_2SiO_3 + BaTiO_3 \leftarrow Na_2TiO_3 + BaSiO_3$
22	K, Ba $\|$ SiO_3, TiO_3	$K_2SiO_3 + BaTiO_3 \leftarrow K_2TiO_3 + BaSiO_3$
23	Li, Ba $\|$ SiO_3, TiO_3	$Li_2SiO_3 + BaTiO_3 \leftarrow Li_2TiO_3 + BaSiO_3$
24	Na, Ba $\|$ CO_3, TiO_3	$Na_2CO_3 + BaTiO_3 \leftarrow Na_2TiO_3 + BaCO_3$
25	K, Ba $\|$ CO_3, TiO_3	$K_2CO_3 + BaTiO_3 \leftarrow K_2TiO_3 + BaCO_3$
26	Pb, Ba $\|$ BO_2, TiO_3	$Pb(BO_2)_2 + BaTiO_3 \leftarrow PbTiO_3 + Ba(BO_2)_2$

26 systems in all were investigated, consisting of diagonal sections of ternary reciprocal systems with the participation of barium titanate. These systems are set forth in Table 1, in the left portion of the equations.* The two binary systems: $BaTiO_3$ with $BaCl_2$ and Na_2TiO_3 were also investigated. The fusion data and character of the crystals formed permitted us to establish that 19 of the 26 systems investigated were stable diagonal sections of reciprocal systems. This means that there is no exchange reaction between the components. The experimental data concerning the fusibility of the systems (the solubility of $BaTiO_3$ at various temperatures) are set forth in Table 2.

The very low content (percentages up to 7-8%) of $BaTiO_3$ in the eutectic compositions appears to be characteristic of stable diagonal sections with barium titanate. (The systems $Li_2SiO_3-BaTiO_3$ and $Na_2SiO_3-BaTiO_3$ where respectively 16 and 27% $BaTiO_3$ enter into the composition of the eutectic mixtures, constitute an exception). This is evidence that the exchange reaction of the indicated sections is markedly displaced in the direction of the starting materials. The latter also graphically illustrates the reciprocal systems Na, Ba $\|$ Cl, TiO_3 and Na, Ba $\|$ TiO_3, CO_3 previously investigated by us, in which the field of $BaTiO_3$ occupies up to 99% of the entire area, while the isotherms intersect on the diagonal at an acute angle which even indicates a

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* The fusion curves of $BaTiO_3$ with the silicates of sodium, potassium and lithium were obtained by G. A. Bukhalova.

TABLE 2

Column 1 –% $BaTiO_3$; Column 2 – Temperature at Which the First Crystals Appear. (E – Eutectic, P – Intersection of the branches of crystallization)

$Na_2F_2-BATiO_3$

1	2
0.0	982
0.5	975
1.0	971
3.0	967
5.0	961
7.0	955
7.5	970
8.0	1000
8.5	1010
9.0	1023
11.0	1080

E at 952° and 7% $BaTiO_3$

$K_2F_2-BaTiO_3$

1	2
0.0	856
0.5	847
1.0	838
2.0	826
3.0	818
4.0	834
5.0	855
6.0	894
6.5	920
7.0	932
7.5	960
8.0	974
9.0	1000
10.0	1034
12.0	1100

E at 814° and 3.5% $BaTiO_3$

$(NaVO_3)_2-BaTiO_3$

1	2
0.0	640
0.5	635
1.0	630
2.0	620
2.5	611
3.0	625
3.5	668
4.0	720
4.6	752
5.5	770
6.0	780
7.0	810
8.0	840
9.0	871
10.0	884
11.0	904
12.0	919
13.0	930
14.0	939
16.0	960
19.0	990

E at 611° and 2.5% $BaTiO_3$

$(KVO_3)_2-BaTiO_3$

1	2
0.0	520
0.5	508
1.0	500
1.5	559
2.0	602
2.5	612
3.0	630
3.5	659
4.0	687
5.0	712
5.5	722
6.0	728
7.0	760
7.5	774
9.0	810
10.0	834
11.5	856
14.0	900
15.0	922

E at 500° and 1% $BaTiO_3$

$Na_2SiO_3-BaTiO_3$

1	2
0.0	1086
3.0	1076
6.0	1058
9.0	1045
14.0	1025
19.0	998
23.0	974
25.0	958
29.0	969
32.0	1016

E at 942° and 27% $BaTiO_3$

$K_2SiO_3-BaTiO_3$

1	2
0.0	976
2.0	934
4.0	922
6.0	958
9.0	988
12.0	1013
15.0	1028
20.0	1054

E at 900° and 3% $BaTiO_3$

$Li_2SiO_3-BaTiO_3$

1	2
0.0	1200
14.0	1100
16.0	1062
18.0	1072
20.0	1090

E at 1048° and 16% $BaTiO_3$

$Na_2CO_3-BaTiO_3$

1	2
0.0	857
0.25	852
0.50	844
0.75	840
1.0	834
1.25	830
1.50	880
1.75	980

E at 826° and 1.4% $BaTiO_3$

$K_2CO_3-BaTiO_3$

1	2
0.0	896
0.25	890
0.50	883
0.75	878
1.00	890
1.25	950
1.50	1000
1.75 up to	1100
(did not dissolve)	

E at 873° and 0.9% $BaTiO_3$

$(NaPO_3)_2-BaTiO_3$

1	2
0.0	619
0.4	580
0.7	580
1.5	610
2.3	726
3.0	752
3.8	796
4.5	830
6.0	850

E at 580° and 0.7% $BaTiO_3$

$Pb(PO_3)_2-BaTiO_3$

1	2
0.0	616
0.25	616
0.50	614
1.0	630
1.5	662
2.0	708
2.5	746
3.0	780
3.5	820
4.0	854

E at 613° and 0.7% $BaTiO_3$

$Na_2SO_4-BaTiO_3$

1	2
0.0	885
0.25	870
0.50	940
0.70	990
1.00 up to	1200
(did not dissolve)	

E at 868° and 0.3% BaTiO3

$Li_2SO_4-BaTiO_3$

1	2
0.0	860
0.25	854
0.50	900
0.75	980
1.0 up to	1000
(did not dissolve)	

E at 849° and 0.4% $BaTiO_3$

$K_2MoO_4-BaTiO_3$

1	2
0.0	920
0.25	914
0.50	928
0.75	984
1.00	1040

E at 909° and 0.4% $BaTiO_3$

$K_4P_2O_7-(BaTiO_3)_2$

1	2
0.0	1099
5.0	1060
7.0	1042
10.0	1022
11.0	992
12.0	1004
14.0	1020
16.0	1040
20.0	1080
22.0	1100

P at 992° and 11% $BaTiO_3$

$Na_4P_2O_7-(BaTiO_3)_2$

1	2
0.0	994
0.5	992
1.0	989
1.6	979
2.0	969
2.5	959
3.5	954
4.5	948
5.0	938
5.5	932
6.0	923
6.5	908
7.0	897
7.5	892
8.5	888

TABLE 2 (Continued)

1	2
$Na_4P_2O_7-(BaTiO_3)_2$	
9.5	878
11.0	868
12.0	857
13.0	857
13.5	867
14.0	888
14.5	903
15.0	918
15.5	953
16.0	974
16.5	999
17.0	1014
18.0	1028
P at 853° and 13% $BaTiO_3$	
$Pb_3(PO_4)_2-(BaTiO_3)_3$	
0.0	1014
0.5	1004
1.5	995
2.5	986
3.5	980
5.0	967
6.5	968
8.0	966
9.0	968
10.0	986
12.5	1014
16.0	1040
18.0	1056
P at 623° and 9% $BaTiO_3$	

1	2
$Pb(BO_2)_2-BaTiO_3$	
0.0	686
2.0	658
6.0	634
10.0	688
15.0	752
20.0	816
25.0	870
30.0	925
35.0	970
P at 623° and 5% $BaTiO_3$	
$(KPO_3)_2-BaTiO_3$	
0.0	806
2.0	776
4.0	760
6.0	748
7.0	747
10.0	746
11.0	746
13.0	746
14.0	746
17.0	752
18.0	756
19.0	762
20.0	766
21.0	768
22.0	772
23.0	776
24.0	786
25.0	802
26.0	816

1	2
$(KPO_3)_2-BaTiO_3$	
27.0	838
28.0	858
29.0	878
30.0	898
31.0	918
33.0	943
33.5	960
35.0	990
P_1 at 746° and 11% $BaTiO_3$	
P_2 at 747 and 16% $BaTiO_3$	
P_3 at 776° and 24% $BaTiO_3$	
$Na_2MoO_4-BaTiO_3$	
0.0	690
0.25	683
0.50	805
0.75	900
1.00	938
1.25	966
1.50	994
1.75 up to	1000
(did not dissolve)	
P at 678° and 0.3% $BaTiO_3$	
$Na_2WO_4-BaTiO_3$	
0.0	695
0.25	816
0.50	980

1	2
$Na_2WO_4-BaTiO_3$	
0.75	1028
1.0	1040
$BaCl_2-BaTiO_3$	
0.0	964
0.25	960
0.50	955
0.75	945
1.0	941
1.25	936
1.50	931
1.75	926
2.0	924
2.25	922
2.5	920
2.75	916
3.0	919
3.25	908
3.5	906
3.75	903
4.0	903
4.25	922
4.5	941
4.75	958
5.0	974
$Na_2TiO_3-BaTiO_3$	
0.0	1045
1.0	1012
2.0	1004
3.0	996
4.0	989
5.0	1000
6.0	1040

singular character for the systems. In connection with this the abrupt gradient of the branch of crystallization of $BaTiO_3$ is of interest in the stable sections under investigation; it is possible that, in the region of greatest concentrations of barium titanate and high temperatures, stratification of the components in the liquid state occurs. The systems formed by $BaTiO_3$ with the pyrophosphates of potassium and sodium, sodium tungstate, potassium metaphosphate, sodium molybdate, lead orthophosphate and metaborate do not appear to be stable sections of the corresponding reciprocal systems. The high fusion temperatures of the salts did not permit us to establish whether in these systems chemical compounds are formed or exchange products separate out.

The experimental material obtained indicates that barium titanate is a substance which is slightly soluble in the majority of salt melts. The best solvents (at 1000-1100° from 6 to 40% of $BaTiO_3$ is dissolved) appear to be the silicates of lithium, sodium and potassium, the fluorides of sodium and potassium, potassium metaphosphate, sodium and potassium metavanadates, sodium and potassium pyrophosphates, lead orthophosphate and metaborate. The poorest solvents (at 1000° from 0.5 to 6% $BaTiO_3$ dissolved) appear to be carbonates of sodium, potassium and barium, and the metaphosphates of sodium and lead. Sodium sulfate and the molybdates of the alkaline metals are poor solvents (0.5 to 1.5% $BaTiO_3$ dissolved at 1000°). $BaTiO_3$ hardly dissolved at all(even in portions of tenths of a percent)in potassium sulfate, the chlorides of the alkali metals and in lithium fluoride.

It is evident from the data set forth that eutectic mixtures (Table 2) are formed in the majority of cases in diagonal sections of ternary reciprocal systems with the participation of barium titanate. This provides the possibility of utilizing the systems under study to select advantageous solvents for growing monocrystals of barium titanate from fused media.

It is practically and theoretically important to elucidate the general pattern of the reactions in reciprocal systems with the participation of barium titanate; with the aid of this it would be possible in advance to have a representation of the chemistry of the processes which proceed during the sintering of certain ceramic materials containing barium titanate and also concerning the solubility of barium titanate, in various salt melts.

On account of the absence of data on the heat of formation of titanates, we cannot take advantage of the well-known rule which, in the absence of pronounced complex formation, makes it possible to judge the direction of the exchange reaction in reciprocal systems by the magnitude of the conventionally calculated heat effect of the reaction [4]. An attempt to extend to systems with the participation of barium titanate the Palkin's rule [5] to the effect that equilibrium in reciprocal systems is displaced in the direction of the most highly fusible component, and the rule of Gustavson-Beketov [6] concerning the tendency of the smaller ions to unite with the smaller and the larger, with the larger gives interesting results.

It turned out that Palkin's hypothesis and the Gustavson-Beketov rule applied very well to the majority of the systems which were studied. Thus, Palkin's hypothesis is quite justified for all systems which have a stable character and is not vindicated for systems on the fusion curves of which either exchange products, or chemical compounds arise [$BaTiO_3$ in combination with Na_2WO_4, Na_2MoO_4, $Na_4P_2O_7$, $K_4P_2O_7$, KPO_3, $Pb_3(PO_4)_2$, $Pb(BO_2)_2$]. Deviations from Palkin's thesis were also observed previously in a whole series of systems with sharply expressed complex formation, such as, for example: Li, K ‖ SO_4, PO_3 [7]; Li, K ‖ SO_4, NO_3 [8]; Li, Sr ‖ F, Cl; Na, Ba ‖ F, Cl [9]; Li, Ba ‖ F, Cl [10]; Ca, Ba ‖ F, Cl [11] and others. This makes it possible to confirm that Palkin's thesis is generally applicable only to systems without complex formation or where the complex formation is slight. In accord with this, deviations from Palkin's rule in systems including $BaTiO_3$ are probably due to chemical reaction within the reciprocal systems.

Of the 26 sections investigated by us, only the systems $BaTiO_3$ with: $(KPO_3)_2$, $Pb_3(PO_4)_2$, $Pb(BO_2)_2$, K_2MoO_4, Na_2SO_4, K_2SO_4, Li_2SO_4 deviate from the Gustavson-Beketov rule. It is pertinent to note here that the direction of the exchange reaction found on the basis of the magnitude of the conventionally calculated heat effect often does not agree with the thesis of Palkin and the Gustavson-Beketov rule. This is characteristic in those cases in which chemical compounds are formed in the systems. The reaction $Na_2Cl_2 + BaF_2 = 2NaF + BaCl_2$ can serve as an example. According to Palkin's thesis and the conventionally calculated heat effect the equilibrium of the exchange reaction should be displaced toward $Na_2Cl_2-BaF_2$; according to the Gustavson-Beketov rule, on the contrary, toward $Na_2F_2-BaCl_2$. Actually the diagonal $Na_2Cl_2-BaF_2$ intersects the field of a stable chemical compound $BaCl_2 \cdot BaF_2$.

It is noteworthy that of the 26 diagonal sections with the participation of $BaTiO_3$, systems deviate from the thesis of Palkin in which participate an oxygen-containing anion, anions containing elements with incomplete electron shells (WO_4, MoO_4), anions inclined toward polymerization (PO_3, PO_4), and also cations with an 18 electron shell (Pb).

An attempt to extend to systems including barium titanate the recently proposed hypothesis to the effect that one of the factors facilitating the growth of irreversibility and consequently, the diminishing mutual solubility of salts of stable pairs, is the great difference in the polarizability of cations and anions [12], demonstrated that this hypothesis is justified only for the fluorides of the alkaline metals. $BaTiO_3$ is almost completely insoluble in lithium fluoride and is comparatively quite soluble in the fluorides of Na and K. This order of solubility is not observed in all the other systems, in spite of the fact that according to the polarizability of the ions: Li-0.03, Na-0.19, K-0.89, Ba-1.86, it should be observed in all cases. Analysis of the results obtained permits us to conclude as a first approximation that the solubilities of barium titanate in melts of various salts of Li, Na, K, and Pb are to a larger extent determined by the character of the anions than by that of the cations.

Inasmuch as the conventionally calculated thermal effect of the reaction is determined for room temperature, it cannot furnish a representation of the thermal effect of the reaction in the fused state; the fusion temperature of the salts and the radii of the ions cannot encompass every multiform system; they are justified only for the most simple systems consisting of ions with complete electron shells and not complicated with chemical reactions within the reciprocal system.

The solubility of the salts and the direction of the binary exchange reaction in the fused state are determined by the combination of a whole series of properties depending on the position of the elements in the Mendeleev periodic table (the structure of the inner electron shells, the polarizability, the radius of the ions, etc.). It appears to us that the character of the chemical bond in compounds most completely reflects the entire aggregation of properties of the elements; it is, therefore, necessary to take precisely this factor into account in the basic classification of reciprocal systems. Unfortunately, the quantitative evaluation of the character of the chemical bond is difficult for many compounds; none the less, it can be seen from the vast experimental material on the solubility of salts in fused media and from exchange reactions that the equilibrium is always displaced in the direction of pairs of compounds which are markedly different from each other in the character of the chemical bond and the more marked this difference, the more the system will approach to the irreversible – singular type and the less will be the mutual solubility of salts of the stable pair. On the other hand, when the character of the bonds of the pair of salts is close, the system will always be reversible and the mutual solubility will be maximum. This conclusion is in excellent agreement with the long known rule: like dissolves in like.

Data concerning the solubility of barium titanate in various fused media are in excellent agreementwith this: $BaTiO_3$ crystallizes in the perovskite pattern and consists of a continuous three dimensional anion consisting of regular or deformed (TiO_6) octahedra with a Ti ion in the center. Ba ions are located in the spaces between these octahedra [13]. In compounds of a similar type, for example $PbTiO_3$, $CaTiO_3$, $SrTiO_3$ and others, barium titanate not only dissolves in the fused state, but also yields solid solutions. The relatively good solubility of $BaTiO_3$ in silicates, metaphosphates and borates is, therefore, also comprehensible; it is characterized by the highly polymerized molecular structure.

The peculiar position which the fluorides of sodium and potassium occupy in the series of excellent solvents of barium titanate is of interest. Sodium and potassium fluorides crystallize in an ionic lattice of the NaCl type, and none the less appear to be some of the best solvents of $BaTiO_3$, while $BaTiO_3$ is almost completely insoluble in the other halides of the alkaline metals. The excellent solubility of barium titanate in fluorides is apparently associated with partial substitution of oxygen ions by fluorine ions and, consequently, with weakening of the bond of titanium with oxygen.

SUMMARY

1. The fusion diagrams of barium titanate with fluorides, silicates, carbonates, pyro- and metaphosphates, metaborates, chlorides, molybdates, sulfates, tungstates of the alkaline and certain divalent metals were investigated up to 1200°.

2. It was established that of the 26 systems investigated, representing diagonal sections of ternary reciprocal systems, 19 were stable sections (Table 1) and can be utilized for cultivating monocrystals of $BaTiO_3$ from the fused media.

3. It was established that $BaTiO_3$ is poorly soluble in the majority of salt melts of Na, K, Li, Pb, and Ba.

4. It was shown that the character of the chemical bond as maximally reflecting the entire aggregate of properties of the elements, should be the basis for the classification of ternary reciprocal systems and of the theory of the solubility of salts in fused media.

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**** See Consultants Bureau Translation, page 1721.
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[illegible] salts in fused melts and from exchange reactions that the equilibrium is always displaced in the direction of pairs of compounds which are markedly different from each other in the character of the chemical bond and the more marked this difference, the more the system will approach to the irreversible-reciprocal type and the [illegible] will be the mutual solubility of salts in the liquid state. On the other hand, when the character of the bonds of the pair of salts is similar, the system [illegible] reversible and the mutual solubility [illegible]. The [illegible] agreement with the long-known rules, [illegible].

Data concerning the solubility of [illegible] in various fused salts are in excellent agreement with [illegible] $BaTiO_3$ crystallizes [illegible] the perovskite pattern and [illegible] of [illegible] octahedra (TiO$_6$) [illegible] with a Ti ion in the center [illegible] [13]. In compounds of a similar type, for example $PbTiO_3$, $CaTiO_3$, $SrTiO_3$ and others [illegible] in the fused state, but [illegible] with solutions. [illegible] perovskites and borates [illegible] constituents [illegible].

The peculiar position which the fluorides of sodium and potassium occupy in the series of [illegible] of barium titanate is of interest. Sodium and potassium fluorides [illegible] in an ionic lattice of the NaCl type [illegible] appear to be among the best solvents of $BaTiO_3$, while in NaCl [illegible] in the other halides of the alkali metals. The exceptional solubility of barium titanate in fluorides is apparently associated with partial substitution of oxygen ions by fluorine ions [illegible] of titanium with oxygen.

SUMMARY

1. The fusion diagrams [illegible] of barium titanate with fluorides, chlorides, bromides, iodides and [illegible] sodium, potassium, [illegible] were [illegible] up to 1200°.

2. [illegible]

3. It was established that $BaTiO_3$ is poorly soluble in the majority of salt melts [illegible].

4. It was shown that the character of the chemical bond [illegible] of the solubility of salts in fused melts.

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CRACKING OF NORMAL PARAFFINIC HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE

I. CRACKING OF n-HEPTANE AND n-NONANE

L. A. Potolovsky and G. S. Spektor

The object of the present work is to study the influence of the magnitude of the molecular weight of the initial normal paraffinic hydrocarbon and the conditions of cracking in the presence of aluminum chloride on the composition of the end products of the cracking, and to specify the composition of these products.

A considerable amount of work has been devoted to the cracking of individual low molecular weight paraffinic hydrocarbons of normal structure in the presence of aluminum chloride. The action of halogen salts of aluminum on paraffinic hydrocarbons of normal structure was studied for the first time by Gustavson in 1881 [1, 2]. Moldavsky [3-6] and also other investigators [7-14] conducted significant investigations in this field. As a result of the study of the cracking of individual normal paraffinic hydrocarbons from C_5 to C_8 in the presence of $AlCl_3$ at atmospheric pressure and at temperatures not exceeding the boiling point of the initial hydrocarbons, it was established that the basic reaction products formed were iso-paraffinic hydrocarbons with both less and greater numbers of carbon atoms in the molecule than in the initial hydrocarbon, and also isomers of the latter. Naphthenic, aromatic and unsaturated hydrocarbons were absent in the reaction products (in the hydrocarbon layer, not bound to $AlCl_3$).

In the work [15-18] on the cracking of normal paraffinic hydrocarbons with a carbon atom content of C_9 and up, the products formed as a result of the reaction have hardly been characterized at all. It has only been established that the butane fraction always predominates in the gaseous products. The liquid products have either not been investigated at all or have been characterized only as low molecular weight paraffinic hydrocarbons without indications as to their structure.

We studied the cracking of n-heptane, n-nonane, n-hexadecane and technical paraffin using the latest methods for investigating the reaction products.

EXPERIMENTAL

The study of the cracking reaction of n-heptane was carried out at temperatures of 50 and 93.5° with 10 and 20% $AlCl_3$, while that of nonane was carried out in the presence of 10% $AlCl_3$ at temperatures of 100 and 150°. The beginning of the formation of so-called "complex" compounds of the hydrocarbons and $AlCl_3$ (the lower dark colored layer) was accompanied in all cases by the cracking of the initial hydrocarbon with evolution of gas.

The characteristics of the initial individual hydrocarbons are set forth in Table 1.

TABLE 1

Characteristics of the Initial Hydrocarbons

Hydrocarbon	Boiling point (in °)		d_4^{20}		n_D^{20}	
	Our data	Literature data [19]	Our data	Literature data [19]	Our data	Literature data [19]
n-Heptane	98.5	98.4	0.6836	0.6839	1.3878	1.3877
n-Nonane	150.7	150.7	0.7177	0.7180	1.4060	1.4056

Sublimated aluminum chloride with the following characteristics: $AlCl_3$ 98.37%, $FeCl_3$ 0.05%, residue 1.58% was used in the study of the cracking of the hydrocarbons indicated above.

The experiments were carried out at atmospheric pressure in the presence of hydrogen chloride as an accelerator in the laboratory apparatus depicted in the figure. Hydrogen chloride was continuously supplied to the reaction zone.

The reaction products being formed, together with HCl were continuously conducted through a column with an electrical heating unit, 400 mm in height and 10 mm in diameter, joined to the reaction vessel. A ring of glass thread 0.5 mm in section served as packing for the column. The diameter of the ring was equal to 2-3 mm.

The temperature regime of the fractionating column was established depending on the initial crackability of the hydrocarbon so that a minimal quantity of unreacted initial hydrocarbon was eliminated from the reaction zone in the stream of gas which was being formed and hydrogen chloride which was introduced into the reaction. For example, during the cracking of n-heptane the temperature of the column was maintained at a level of 50-60° and during the cracking of n-nonane, 80-100°.

The gaseous cracking products were fractionated at low temperatures in a Podbielniak apparatus with subsequent analysis of the fractions obtained. The quantity of isobutane was determined in addition by the method of the critical temperature of solution of the butane fraction in o-nitrotoluene.

The liquid cracking products were subjected initially to stabilization and then to clear-cut rectification in a column with 40 theoretical plates under the operating conditions.

TABLE 2

Balance Sheet of the Cracking Products of n-Heptane and N-Nonane

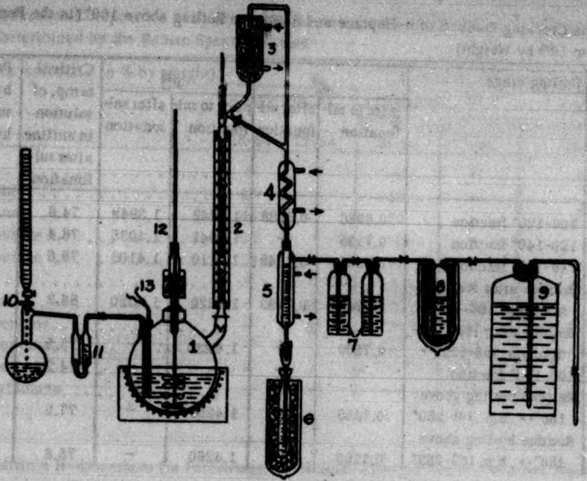
Experimental conditions	Yield, in weight % of the initial hydrocarbon			
	n-Heptane		n-Nonane	
Temperature (in °)	50°	98.5°	100°	150°
Weight percent of $AlCl_3$	10	10	10	10
Total gas	19.8	24.0	19.8	21.0
Iso-C_4H_{10} included in the total gas	19.3	23.1	19.2	19.8
Boiling range of the fractions (in °):				
27-29	8.3	9.3	10.5	11.5
29-38	1.1	0.5	0.6	0.7
38-64	6.7	4.7	4.2	5.7
64-77	1.9	1.2	0.6	0.6
77-94	8.9	2.3	1.3	1.5
94-100	32.2	40.8	0.3[1]	0.6[1]
100-120	3.0	–	1.0[2]	0.8[2]
120-140	2.9	–	1.2[3]	0.5[3]
140-160	2.3	–	39.6[4]	39.5[4]
Residue after rectification	4.9	5.5	4.3	3.9
Hydrocarbons which are bound to $AlCl_3$ and contained in the residue after cracking	8.0	11.7	16.6	13.7
Total percent of hydrocarbon conversion	67.7	59.2	60.4	60.5

Note: The fractions which boiled in the ranges: 1) 94-120°; 2) 120-140°; 3) 140-148°; 4) 148-150° consisted of unreacted n-nonane.

The physical constants (specific gravity, coefficient of refraction, critical temperature of solution in aniline) of the fractions obtained were determined to characterize them; for the fractions boiling below 100° the hydrocarbon composition was also determined by the Raman spectra method.

The balance sheet of the cracking products of n-heptane and n-nonane is set forth in Table 2, while in Tables 3 and 4 are presented the physical constants of the cracking products boiling below 100° and the characteristics of the cracking products boiling above 100°.

It follows from the data of Table 5 that increased reaction temperature during the cracking of n-heptane leads to an increased yield of gas (29.2% at a temperature of 50° and 40.5% at 98.5°, calculating on the basis of the n-heptane which had reacted); increase in the quantity of $AlCl_3$ only accelerates the reaction. Change in the temperature within the limits of 100-150° during the cracking of n-nonane has practically no influence on the total yield of gas, which amounts to 33-34% of the reacting hydrocarbon. The composition of the gaseous cracking products of n-heptane and n-nonane is very close. Isobutane appears to be the basic component of the gas. Unsaturated hydrocarbons are absent in the gas. Small quantities of methane, ethane, propane and an insignificant quantity of water appear as admixtures in the isobutane. The yield of propane is increased with increased cracking temperature. Thus, during the cracking of n-heptane, the yield of propane increases from 0.4% at 50° to 1.5% at its boiling point (98.5°), while during the cracking of n-nonane it increases from 2.3% at 100° to 5.2% at 150°.



Scheme of the laboratory apparatus for cracking hydrocarbons with $AlCl_3$. 1) Reaction flask; 2) column with packing and electrical heating unit; 3) condenser; 4) cooler; 5) receptacle with cooler; 6) ampoule for benzene; 7) absorber for HCl; 8) trap for benzene; 9) gasometer; 10) apparatus for preparing HCl; 11) desiccator for HCl; 12) stirrer; 13) thermocouple.

The data of Table 2 show that the bulk of the liquid cracking products of n-heptane and n-nonane boil in the range 27-100°. The physical constants of the fractions boiling below 100° (Table 3) and their analysis by the Raman spectra method (Table 6) demonstrate that their basic components are isopentane, isohexanes and isoheptanes.

TABLE 3

Physical Constants of the Cracking Products of n-Heptane and n-Nonane Which Boil Below 100°

Hydrocarbon	Temp. of expt. (in °)	$AlCl_3$ (in weight %)	27-29° fraction		29-38° fraction	38-64° fraction		64-77° fraction		77-94° fraction	
			d_4^{20}	n_D^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}
n-Heptane	98.5	20	0.6197	1.3530	–	0.6538	1.3715	0.6675	1.3792	0.6816	1.3865
n-Heptane	50	10	0.6194	1.3536	1.3573	0.6534	1.3715	0.6678	1.3795	0.6814	1.3864
n-Heptane	98.5	10	0.6201	1.3540	1.3557	0.6522	1.3710	0.6674	1.3800	0.6818	1.3861
n-Nonane	100	10	0.6193	1.3530	1.3560	0.6534	1.3730	–	1.3780	0.6819	1.3870
n-Nonane	150	10	0.6196	1.3540	1.3563	0.6538	1.3728	–	1.3780	0.6816	1.3869

The yields of paraffinic hydrocarbons with an iso-structure (in percentages by weight) are calculated on the basis of reacted hydrocarbon in Table 7. As is evident from the data of Table 7, the yields of paraffinic hydrocarbons with an iso-structure formed as a result of the cracking of n-heptane at a temperature of 98° and the cracking of n-nonane at temperatures of 100 and 150° are arranged in diminishing order fom isobutane to isoheptane. During the cracking of n-heptane at 50° the yield of the isoheptane fraction exceeds the yield of the isopentane and isohexane fractions. This is evidently to be explained by the favorable conditions (low temperature) for the isomerization reaction.

The basic cracking products of n-heptane and n-nonane appear to be isoparaffinic hydrocarbons with a methyl group at the second hydrocarbon atom (Table 6); along with isoparaffins with one methyl group in position

TABLE 4

Characteristics of the Cracking Products of n-Heptane and n-Nonane Boiling above 100° (in the Presence of a Quantity of $AlCl_3$ Equal to 10% by Weight)

Hydrocarbon	Temp. of expt. (in °)	Boiling range	d_4^{20}		n_D^{20}		Critical temp. of solution in aniline after sulfonation	Percentage by weight of sulfonated hydrocarbons***
			prior to sulfonation	after sulfonation	prior to sulfonation	after sulfonation		
n-Heptane	50	100-120° fraction	0.6966	0.6968	1.3949	1.3949	74.6	0.0
n-Heptane	50	120-140° fraction	0.7138	–	1.4041	1.4035	76.4	2.4*
n-Heptane	50	140-160° fraction	0.7355	0.7349	1.4110	1.4108	78.6	0.0
n-Heptane	50	Residue after rectification, b.p. 160-298°**	0.7741	0.7733	1.4320	1.4320	84.2	1.5
n-Heptane	98.5	Residue after rectification, b.p. 105-222°**	0.7500	–	1.4230	–	73.5	2.2
n-Nonane	150	100-150° fraction	–	–	–	–	74.2	2.0
n-Nonane	150	Residue boiling above 150°**, b.p. 148-250°	0.7659	–	1.4258	–	77.2	4.0
n-Nonane	100	Residue boiling above 150°**, b.p. 152-253°	0.7662	–	1.4260	–	75.8	3.0

2 or 3, more highly branched isomers with two methyl groups in positions 2, 3, and 2,4 and also isomers with a quaternary carbon atom are formed. It should be noted that during the craking of n-heptane with the temperature of the experiment increased, the yield of the latter is considerably diminished.

TABLE 5

Composition and Yield of the Gaseous Cracking Products of n-Heptane and n-Nonane with $AlCl_3$ (in percentages by Weight)

Characteristic	n-Heptane			n-Nonane	
Temperature (in °)	50	98.5	98.5	150	100
Percentage by weight of $AlCl_3$	10	10	20	10	10
Composition of the gas:****					
CH_4	0.8	1.2	1.8	0.5	0.7
C_2H_6	0.8	1.2	0.4	0.0	0.0
C_3H_8	0.4	1.5	1.9	5.2	2.3
iso-C_3H_{10}	97.5	96.1	95.9	94.3	97.0
n-C_4H_{10}	0.5	0.0	0.0	0.0	0.0
Yield of gas:					
on the basis of the initial hydrocarbon	19.8	24.0	31.0	21.0	19.8
on the basis of the hydrocarbon which reacted	29.2	40.5	40.2	34.7	32.9

The quantity of products boiling above 100° which is formed during the cracking of n-heptane depends on the reaction temperature. Low experiment temperatures facilitate the formation of high boiling hydrocarbons while at higher temperatures their yield is diminished (Table 2).

This phenomenon can apparently be explained by the destructive alkylation reaction which takes place during the cracking of paraffinic hydrocarbons in the presence of $AlCl_3$ [9] and proceeds more appreciably under low temperature conditions.

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* The specific dispersivity of the fraction was equal to 100.6

** The boiling range of the residues was determined by redistilling them from a Würtz flask 5 ml in capacity.

*** The sulfonation was carried out with three volumes of 98% H_2SO_4.

**** An insignificant quantity of hydrogen (0.01-0.02%) was contained in the gas.

TABLE 6

Individual Hydrocarbon Composition of the Fractions Formed During the Cracking of n-Heptane and n-Nonane with 10% $AlCl_3$ as Determined by the Raman Spectra Method*

Hydrocarbon composition (in % by weight)	Hydrocarbon, and temperature of the experiment						
	n-Heptane, 50°		n-Heptane, 98.5°		n-Heptane**	n-Nonane, 150°	
	Boiling range of the fractions (in °)						
	38-64	77-94	38-64	77-94	64-77	27-38	38-64
Isopentane	–	–	–	–	–	100	–
2-Methylpentane	27	–	48	–	–	–	68
3-Methylpentane	45	–	20	–	18	–	20
2,2-Dimethylbutane	20	–	12	–	–	–	–
2,3-Dimethylbutane	8	–	10	–	–	–	–
n-Hexane	–	–	–	–	11	–	12
2-Methylhexane	–	35	–	40	–	–	–
2,4-Dimethylpentane	–	35	–	18	50	–	–
2,3-Dimethylpentane	–	–	–	16	–	–	–
2,2-Dimethylpentane	–	–	–	–	8	–	–
2,2,3-Trimethylbutane	–	30	–	26	12	–	–

TABLE 7

Yield of Isoparaffinic Hydrocarbons (in Percentages by Weight) Based on the Hydrocarbon Which Reacted (in the Presence of a Quantity of $AlCl_3$ Equal to 10% by Weight)

Hydrocarbon	Temperature (in °)	Isobutane	2-Methylbutane (isopentane)	Isohexanes	Isoheptanes
n-Heptane	50	28.5	13.8	10.4	15.1
	98.5	39.0	16.5	8.3	5.3
n-Nonane	100	31.9	18.4	6.3	2.8
	150	32.7	20.1	8.5	3.1

TABLE 8

Influence of Hydrogen Chloride on the Cracking of n-Heptane

Hydrocarbon	Yield in % by weight			
	In the presence of HCl		In the absence of HCl	
	Based on the initial n-heptane	Based on the n-heptane which reacted	Based on the initial n-heptane	Based on the n-heptane which reacted
Isobutane	23.1	39.0	5.2	27.0
Isopentane	9.8	16.5	2.5	13.2
Isohexanes	4.9	8.3	2.4	12.7
Isoheptanes	3.1	5.3	2.0	10.6
Hydrocarbons which are bound to $AlCl_3$ in the residue after cracking	11.7	19.8	1.8	9.1
Total percentage of conversion	59.2		19.4	

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* The hydrocarbon composition of the fractions was determined in the molecular spectroscopy laboratory of the Moscow State University under the direction of V. M. Tatevsky.

** All the 64-77° fractions which were formed during the cracking of n-heptane in all the experiments were combined, since the physical constants of these fractions were very close.

Investigation of the high boiling cracking products of n-heptane and n-nonane showed that they basically consist of paraffinic hydrocarbons (Table 4).

The accelerating action of hydrogen chloride on the cracking reaction of n-heptane in the presence of $AlCl_3$ is shown in Table 8. It follows from the data of the table that the presence of HCl accelerates the cracking reaction by a factor of 3. The presence of HCl also influences the composition of the reaction products.

In the absence of HCl the yield of isobutane is considerably reduced, the yield of isopentane is somewhat lower, the yield of the isohexane fraction is increased by 4.5% and the yield of the isoheptane fraction is doubled (calculated on the basis of the hydrocarbon which reacted).

SUMMARY

1. The basic cracking products of n-heptane at 50 and 98.5° and n-nonane at 100 and 150° (which we have studied in detail for the first time) in the presence of 10% $AlCl_3$ and with the use of HCl as an accelerator are isobutane (32-39%), isopentane (14-20%), isohexanes (6-10%) and isoheptanes (3-5%).

2. Isomers with a methyl group at the second hydrocarbon atom are predominately formed, and in lesser quantity hydrocarbons with a methyl group in position 3, and more highly branched isomers with two methyl groups in positions 2,3, and 2,4 and isomers with a quaternary carbon atom. Paraffinic hydrocarbons with a normal structure are formed in insignificant quantities.

3. The gaseous cracking products basically consist of isobutane (94-97%) and contain insignificant quantities of methane (0.02-1.8%), ethane (up to 1.5%), propane (up to 5%) and hydrogen (hundredths of a percent).

4. Hydrocarbons boiling above 100° are formed in small quantities; according to their chemical structure they consist of paraffinic hydrocarbons.

5. The percent of conversion of n-heptane is increased by a factor of three by the use of hydrogen chloride as a cracking accelerator with other experimental conditions being kept equal. In the absence of HCl the yield of isobutane and isopentane is decreased and the yield of the isohexane and isoheptane fractions is increased.

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INVESTIGATIONS IN THE FIELD OF ALCOHOL OXIDES (OXIDOLS)

II. PREPARATION AND PROPERTIES OF α,β-ALCOHOL OXIDES OF THE ALIPHATIC SERIES

V. I. Pansevich-Kolyada and L. A. Kureichik

The properties of alcohol oxides in which the hydroxyl group is in the α,β- position to the oxide ring, have still hardly been studied at all.

N. A. Prilezhaev [1] in his classic investigations of α-oxides, cites three examples of alcohol oxides which he obtained by oxidizing allyl alcohol, geraniol and linalool with perbenzoic acid. The oxide of allyl alcohol, previously obtained by other routes [2], was readily hydrated in glycerin [3], while the hydration of geraniol and linalool dioxides proceeded only at the oxide ring more distant from the hydroxyl group with the formation of glycerin oxides [4]. On this basis, N. A. Prilezhaev notes that the oxide ring of α,β-alcohol oxides is stabilized by the hydroxyl group while he referred the ready hydration of the oxide of allyl alcohol to the general rule that the first representative of a series differs from its homologs.

However, the oxides of methylstyrylcarbinol and ethylstyrylcarbinol obtained by T. E. Temnikova and V. A. Kropachev [5] by the hydrogenation of the oxides of benzalacetone and phenylpropionylethylene also readily underwent hydration with the formation of the corresponding substituted glycerins.

We obtained the α,β-alcohol oxide, 2-methyl-4-phenyloxido-2,3-pentanol- which has very interesting properties [6] by the oxidation of 2-methyl-4-phenylpenten-2-ol-4 by peroxyacetic acid. On heating in acidified water at room temperature in a desiccator over H_2SO_4, P_2O_5, $CaCl_2$ it, like certain pinacols [7] and benzalacetone oxide [4], is cleaved into acetophenone and isobutylene oxide. The latter is isomerized in the presence of acidic reagents, or by heating, into isobutyric aldehyde, the presence of which was established in the reaction products together with acetophenone. The cleavage of the alcohol oxide proceeds in air and in an alkaline medium, but considerably more slowly. In a semicarbazide solution it is always only acetophenone semicarbazone that is obtained, which indicates the absence of isomerization of the isobutylene oxide, which forms into isobutyraldehyde under these conditions.

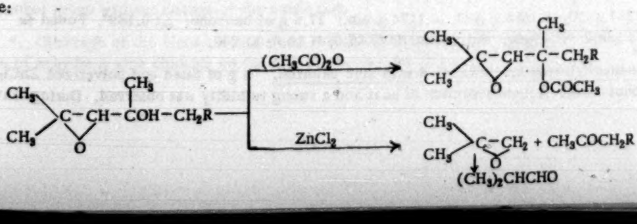
Thus, even these isolated examples of α,β-alcohol oxides show that the properties of these substances are far from being identical.

In the present work, we carried out the oxidation of 2,4,5-trimethylhexen-2-ol-4 and 2,4-dimethyldecen-2-ol-4 with peroxyacetic acid and studied certain properties of the α,β-alcohol oxides thereby obtained.

The oxidation of both alcohols was carried out with 80-92% peroxyacetic acid in absolute ether at a temperature of 20-25°. The reaction proceeded energetically and two α,β-alcohol oxides were obtained as a result – 2,4,5-trimethyloxid-2,3-hexanol-4 and 2,4-dimethyloxido-2,3-decanol-4.

They were rather mobile, colorless liquids with an odor reminiscent of the initial tertiary alcohols. Like the α-oxides they displaced iodine from a neutral potassium iodide solution. In other reactions, however, they markedly differed from the α-oxides of ethylenic hydrocarbons. The latter, as is well known [8], are acetylated at the oxide ring by the action of acetic acid and acetic anhydride, with the formation of mono- and diacetates of glycols, while the alcohol oxides obtained by us are acetylated at the alcoholic hydroxyl group with retention of the oxide ring when heated with acetic anhydride.

A still more marked difference is observed during the action of anhydrous zinc chloride on the alcohol oxides. Depending on the location of the oxide ring, α-oxides [9] are ordinarily isomerized by the action of this reagent into aldehydes or ketones. During the action of anhydrous zinc chloride on the α,β-alcohol oxides obtained by us, the latter are cleaved like 2-methyl-4-phenyloxido-2,3-pentanol-4 [6] into isobutyraldehyde and the corresponding ketone:



The isobutyraldehyde and isobutyric ketones were determined by us as their derivatives with 2,4-dinitrophenylhydrazine, while isobutyraldehyde was also determined as its adduct with dimedone.

Cleavage proceeded most readily for 2,4,5-trimethyloxido-2,3-hexanol-4 which formed the hydrazones of isobutyraldehyde and methylisopropyl ketone even at ordinary temperatures in a hydrochloric acid aqueous solution of 2,4-dinitrophenylhydrazine.

Further study of these interesting compounds will show whether the cleavage of α,β-alcohol oxides under the action of zinc chloride which we have accomplished is a general property of these alcohol oxides, or whether this phenomenon is characteristic only of α,β-alcohol oxides of a specific structure.

We propose in the future, along with retention of the name alcohol oxides, to call these substances oxidols. The term oxidols, which can be extended to substances having several oxide rings or hydroxyl groups, more fully reflects the functional peculiarities of this series.

EXPERIMENTAL

I. Oxidation of 2,4-5-Trimethylhexen -2-ol-4 by Peroxyacetic Acid.

The alcohol was synthesized from isopropylmagnesium bromide and mesityl oxide:

b.p. 56-57° at 7 mm [10]; n_D^{20} 1.4500; d_4^{20} 0.8542; MR_D 44.67; calculated 43.08.

32.6 g of 92% peroxyacetic acid was slowly added to 55 g of the alcohol in 130 ml of absolute ether. The oxidation proceeded rather calmly; the temperature was kept equal to 20-25°. 2.79 g of unreacted peroxyacetic acid was left on the second day and this quantity hardly changed during 4 days, which indicated the end of the reaction. The acetic acid was neutralized with a soda solution and then with dry soda, and the ethereal layer was separated; the acidification products remaining were extracted with ether and the ethereal solution dried over $MgSO_4$. 46 g of substance with a b.p. of 69-70° was obtained by distillation at 8 mm. This was a readily mobile colorless liquid with a camphor odor. The alcohol oxide was readily oxidized with a 1% solution of permanganate, dissolved in cold water and organic solvents, and displaced iodine from potassium iodide. The semicarbazone was not obtained.

n_D^{20} 1.4340; d_4^{20} 0.9217; MR_D 44.64; calculated 44.34.

0.1586 g sub.: 0.3984 g CO_2; 0.1627 g H_2O. 0.2128 g sub.: 26.89 ml CH_4 (0°, 760 mm). 0.1124, 0.2126 g sub.: 19.4 g of benzene: Δt 0.191, 0.371°. Found %: C 68.51; H 11.74; OH 9.65; M 152.4, 151.8. $C_9H_{18}O_2$. Calculated %: C 68.29; H 11.47; OH 10.75; M 158.1.

A yellow-orange crystalline precipitate of the hydrazone was instantaneously formed with 2,4-dinitrophenylhydrazine. Two 2,4-dinitrophenylhydrazones were obtained by fractional crystallization from ethyl alcohol. The first fraction of hydrazone crystals melted at 170-172° and their analysis agreed with that of the 2,4-dinitrophenylhydrazone of isobutyraldehyde.

Found %: N 22.66; M 253.3. $C_{10}H_{12}O_4N_4$. Calculated %: N 22.22; M 252.

The discrepancy between the m.p. and the 2,4-dinitrophenylhydrazone of the isobutyraldehyde obtained by us and that indicated in the literature [11] should be noted.

The last fraction of 2,4-dinitrophenylhydrazone melted at 119-121° [11], and a mixed sample with a known preparation of methylisopropylketone displayed no melting point depression.

Reaction of 2,4,5-Trimethyloxido-2,3-hexanol-4 with Acetic Anhydride. 5 g of the alcohol oxide and 12 g of acetic anhydride were boiled for 12 hours, after which the reaction products were distilled at 9 mm. 1.2 g of substance with a b.p. of 109-112° (9 mm) was isolated. This was a colorless, mobile liquid with a geranium odor which rapidly dissolved in cold water and organic solvents, was readily oxidized by a one percent solution of permanganate, and displaced iodine from potassium iodide. The semicarbazone was not obtained. A test with methylmagnesium iodide demonstrated the absence of active hydrogen.

n_D^{20} 1.4437; d_4^{20} 0.9822; MR_D 54.1; calculated 53.52.

0.1803 g sub.: 0.4327 g CO_2; 0.1583 g H_2O. 0.1174 g sub.: 17.6 g of benzene: Δt 0.189°. Found %: C 65.45; H 9.82; M 189.9. $C_{11}H_{20}O_3$. Calculated %: C 66.0; H 10.0; M 200.

Reaction of 2,4,5-trimethyloxido-2,3-hexanol-4 with zinc chloride. 4 g of fused and pulverized $ZnCl_2$ was added to 15 g of the alcohol oxide. A slight evolution of heat and a strong turbidity was observed. During heating on a water bath at 80-85°, the substance boiled and the liquid over $ZnCl_2$ became completely transparent. The heating was continued for 1.5-2 hours and the volatile products were collected in an alcoholic solution of dimedone. The latter was heated for 4 hours on a water bath; on the following day a crystalline product was obtained which melted at 150-151° [6] after recrystallization from alcohol. No melting point depression was observed in a mixed sample of it with the condensation product of dimedone with isobutyraldehyde.

The zinc chloride was dissolved in water, the reaction products were extracted with ether, dried over $MgSO_4$, and after distilling off the ether were redistilled at ordinary pressure. 2.3 g of substance was isolated which boiled at 97-99° (740 mm). This was a colorless, mobile liquid with a pleasant odor, was readily soluble in organic solvents and in water, and rather rapidly decolorized one percent permanganate solution; active hydrogen was absent.

n_D^{20} 1.3935; d_4^{20} 0.8090; MR_D 25.4; calculated 25.3.

Found %: C 69.08; H 11.70; M 86.11. $C_5H_{10}O$. Calculated %: C 69.76; H 11.62; M 86.

A 2,4-dinitrophenylhydrazone was obtained which melted at 119° after recrystallization from ethanol.

II. Oxidation of 2,4-Dimethyldecen -2-ol-4 with Peroxyacetic Acid

The alcohol was synthesized from hexylmagnesium bromide and mesityl oxide.

B.p. 97° at 5 mm; n_D^{20} 1.4531; d_4^{20} 0.8378; MR_D 59.37; calculated 58.67.

0.1363, 0.1384 g sub.: 0.3945, 0.4001 g CO_2; 0.1603, 0.1624 g H_2O. Found %: C 78.90, 78.90; H 13.10, 13.20. $C_{12}H_{24}O$. Calculated %: C 78.20; H 13.04.

17 g of 80% peroxyacetic acid was gradually added to 33 g of alcohol in 66 ml of dry ether. The reaction proceeded energetically. The temperature of the reaction mixture was kept equal to 20-25°. All the peroxide had reacted after 4 days. The oxidation products were treated as in the preceding case. 15.5 g of substance with a b.p. of 123-124° was obtained by distillation at 6 mm. This was a colorless, rather mobile liquid, with odor resembling hexyl alcohol. The alcohol oxide was insoluble in water and dissolved in organic solvents; it decolorized $KMnO_4$ solution.

n_D^{20} 1.4412; d_4^{20} 0.9003; MR_D 58.60; calculated 58.01.

0.1268 g sub.: 0.3349 g CO_2; 0.1360 g H_2O; 0.1942 g sub.: 20.05 ml CH_4 (0°, 760 mm). 0.0697, 0.1650 g sub.: 20.35 g of benzene: Δt 0.087, 0.193°. Found %: C 72.03; H 12.03; OH 7.88; M 202.4, 215.7. $C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00; OH 8.50; M 200.

Reaction of 2,4-dimethyloxido-2,3-decanol-4 with zinc chloride. 0.4 g of fused $ZnCl_2$ was added to 2.0 g of the alcohol oxide. A marked turbidity of the entire liquid over the zinc chloride was at once observed, but when the liquid was heated on a water bath, as in the preceding case, it became completely transparent. The liquid, which had the odor of rancid fat, was poured off from the precipitate and distilled to 70° into an alcoholic solution of dimedone. Water was poured into the residue which had assumed an almost brown coloration, and a reddish layer thereupon separated which had a rather pleasant odor. A portion of this substance was added to a solution of 2,4-dinitrophenylhydrazine. Orange crystals rapidly settled out which melted at 58-59° after recrystallization from ethyl alcohol; this melting point agreed with that of the 2,4-dinitrophenylhydrazone of methylhexyl ketone [11]. The alcoholic solution of dimedone was heated for 2 hours on a water bath. Crystals precipitated on the next day which melted at 151° after recrystallization from ethanol. A mixed sample of these crystals with the condensation product of dimedone with isobutyraldehyde exhibited no melting point depression.

SUMMARY

1. Two unsaturated tertiary alcohols – 2,4,5-trimethylhexen -2-ol-4 and 2,4-dimethyldecen -2-ol-4 – were oxidized with peroxyacetic acid.

2. Two α,β-alcohol oxides – 2,4,5-trimethyloxido-2,3-hexanol-4 and 2,4-dimethyloxido-2,3-decanol-4 – were prepared.

3. During the action of acetic anhydride on 2,4,5-trimethyloxido-2,3-hexanol-4, acetylation proceeded at the alcohol group without change of the oxide ring.

4. Cleavage of the alcohol oxides into isobutyraldehyde and the corresponding ketones occurred during the action of anhydrous zinc chloride on the α,β-alcohol oxides obtained.

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* See Consultants Bureau Translation, page 1437.
** " " " " " a-197.

THE SYNTHESIS OF CERTAIN β-HYDROXY ACIDS AND THEIR ESTERS

G. M. Borodina

The object of the present work was the synthesis of certain β-hydroxy acids and their esters; to wit: β-hydroxy tridecanoic, β-hydroxypentadecanoic and β-hydroxystearic (β-hydroxyoctadecanoic) acids.

In the literature there are directions only for the preparation of β-hydroxystearic acid along with α,β-octadecenoic acid during the heating of β-bromostearic acid with an alcoholic solution of potassium hydroxide [1]. However, both this reaction and the addition of water to unsaturated acids require the presence of the difficultly accessible α,β- and β,γ-unsaturated acids, and is accompanied by side reactions.

It is also well known that the mutual reaction of esters of halogen-substituted acetic acids with aldehydes in the presence of zinc powder (Reformatsky reaction) proceeds with satisfactory yields of esters of β-hydroxy acids only for aldehydes with a number of carbon atoms in the molecule that does not exceed 10-11 [2, 3].

Therefore, we accomplished the preparation of esters of β-hydroxytridecanoic, β-hydroxypentadecanoic and β-hydroxystearic acids via the reduction of the corresponding esters of β-ketoacids with the aid of aluminum amalgams in a medium of moist ether [4].

The initial β-ketoacid esters had not been described in the literature. There are only references to the preparation of the ethyl ester of β-ketotridecanoic acid from sodium acetoacetic ester and the acid chloride of undecanoic acid; however, this ester was not isolated and was only characterized in the form of the 1-phenyl-3-decyl-5-pyrazolone [5].

The esters of β-ketotridecanoic and β-ketopentadecanoic acids were obtained by us by partial acidolysis of the acylmalonic esters [6].

The ester of β-ketostearic (β-ketooctadecanoic) acid was prepared according to the method of Bowman and Fordham [7].

The acid chloride of palmitic acid was condensed with the monosodium derivative of the mixed benzylethyl ester of malonic acid, yielding the corresponding hexadecanoylmalonic ester. The latter was subjected to debenzylation in the presence of palladinized barium carbonate (5% Pd) and the monoethyl ester of hexadecanoylmalonic acid thereby formed was decarboxylated at 80-100°.

The reduction of the esters of the β-keto acids was accomplished with the aid of aluminum amalgam in a moist ether medium.

The ester of β-hydroxyoctadecanoic acid was not subjected to purification, but was directly saponified to obtain β-hydroxyoctadecanoic acid.

β-Hydroxy acids of the general formulas $RCH(OH)CH_2COOH$, where $R = C_{10}H_{21}$, $C_{12}H_{25}$, $C_{15}H_{31}$ were obtained by saponification of the esters of β-hydroxytridecanoic, β-hydroxypentadecanoic and β-hydroxystearic acid with a water-alcohol solution of potassium hydroxide.

EXPERIMENTAL

Undecanoylmalonic Ester

A mixture of 59 g of malonic ester and 24 ml of anhydrous alcohol in 75 ml of anhydrous benzene was added to 9 g of degreased magnesium shavings which had been activated by heating with crystalline iodine, 27.5 ml of dry benzene and 2.5 ml of anhydrous alcohol. All the magnesium went over into solution in the course of 3-5 hours. 20.7 g of the acid chloride of undecanoyl acid (50%, calculating on the basis of the malonic ester) was added to the cooled solution of magnesiumethoxymalonic ester after the excess alcohol had been distilled off with the benzene (25-30 ml), and the mixture was heated and stirred for 1.5-2 hours. After decomposition with a 5% solution of sulfuric acid and elimination of benzene and malonic ester in a vacuum, the residue (42 g) consisted of raw undecanoylmalonic ester.

Ethyl Ester of β-Ketotridecanoic Acid

42 g of undecanoylmalonic ester was heated with a five-fold quantity of glacial acetic acid (38 g) and with 0.2 g of 98% sulfuric acid (0.22% of the weightof the reagents) for 3 hours on a water bath with a reflux condenser. After eliminating the sulfuric acid in the form of barium sulfate (1 g of barium carbonate was added), the excess acetic acid was distilled off in a vacuum. The residue was separated by vacuum distillation with a fractionating column. The first fraction with a b.p. of 120-145° at 20 mm consisted of methyldecylketone -10.3 g (44%); the second fraction with a b.p. of 128-135° at 1.5 mm −12.55 g (38.5%) appeared to be the ester of β-ketotridecanoic acid. After three-fold redistillation at 1.5 mm, the ester of β-ketotridecanoic acid had the form of a colorless, oily liquid, which gave a dark cherry color with ferrous chloride, b.p. 130-135° at 1.5 mm.

d_4^{20} 0.9254; n_D^{20} 1.4455; MR_D 73.7; calculated 73.15.

3.885 mg sub.: 10.041 mg CO_2; 3.590 mg H_2O. Found %: C 70.48, H 10.85. $C_{15}H_{28}O_3$. Calculated %: C 70.26; H 11.00.

Ethyl Ester of β-Hydroxytridecanoic Acid

15 g of the ester of β-ketotridecanoic acid in 300 ml of moist ether was reduced with 42 g of amalgamated aluminum shavings until a positive reaction with ferrous chloride was no longer observed (48 hours). Aluminum oxide was elminated by filtration and washed and treated with hot alcohol. The solvent was distilled off from the combined filtrates. The residue was vacuum distilled. The ethyl ester of β-hydroxytridecanoic acid purified by a single vacuum redistillation had a b.p. of 166-169° at 10 mm; it was a colorless liquid with a fruity odor. The yield was 5 g (35%).

d_4^{20} 0.9234; n_D^{20} 1.4470; MR_D 74.71; calculated 74.65.

3.231 mg sub.: 8.27 mg CO_2; 3.332 mg H_2O. Found %: C 69.85; H 11.54. $C_{15}H_{30}O_3$. Calculated %: C 69.72; H 11.70.

β-Hydroxytridecanoic Acid

12 ml of a 40% solution of potassium hydroxide was added to 3 g of the ethyl ester of β-hydroxytridecanoic acid, and the mixture was left for 12 hours at room temperature. The β-hydroxytridecanoic acid, obtained by acidification with dilute hydrochloric acid, had after threefold crystallization from petroleum ether, the form of colorless, light plates with a m.p. of 78-79°. The yield was 2 g (74.5%). The substance was soluble in alcohol, acetone and a solution of sodium bicarbonate.

3.646 mg sub.: 9.101 mg CO_2; 3.659 mg H_2O. Found %: C 68.12; H 11.22. $C_{13}H_{26}O_3$. Calculated %: C 67.77; H 11.37.

β-Hydroxypentadecanoic Acid

The tridecanoylmalonic ester was obtained in the same manner as the undecanoylmalonic ester by the reaction of the magnesiumethoxymalonic ester and the acid chloride of tridecanoic acid.

The ethyl ester of β-ketopentadecanoic acid was prepared according to the same method as the ethyl ester of β-ketotridecanoic acid −by the partial acidolysis of tridecanoylmalonic ester. After eliminating the acetic acid the residue was separated by fractional distillation at 0.5 mm. The first fraction with a b.p. of 60-120° and a weight of 8.5 g (37.6%) consisted of methyldodecyl ketone; the 10 g (33.2%) of the second fraction boiled at 125-146°.

After threefold redistillation, the ethyl ester of β-ketopentadecanoic acid had the form of a viscous colorless liquid, which crystallized at a temperature below 20°, gave a sharp reaction for the presence of the keto group with ferrous chloride, and boiled at 137-142° at 0.5 mm.

d_4^{30} 0.923; n_D^{30} 1.4498; MR_D 82,74; calculated 82.32.

3.300 mg sub.: 8.672 mg CO_2; 3.327 mg H_2O. Found %: C 71.71; H 11.28. $C_{17}H_{32}O_3$. Calculated %: C 71 36; H 11.96.

The ethyl ester of β-hydroxypentadecanoic acid was prepared by reduction with aluminum amalgam in moist ether in the same manner as the ethyl ester of β-hydroxytridecanoic acid. It was a colorless, oily liquid with a b.p. of 155-159° at 1.3 mm.

3.631 mg sub.: 9.521 mg CO_2; 3.758 mg H_2O. Found %: C 71.55; H 11.58. $C_{17}H_{34}O_3$. Calculated %: C 71.26; H 11.96.

β-Hydroxypentadecanoic acid was prepared by saponifying the ethyl ester of β-hydroxypentadecanoic acid with a water-alcohol solution of potassium hydroxide in the same manner as β-hydroxytridecanoic acid. After three crystallizations from petroleum ether the substance had the form of thin white flakes with a m.p. of 76-77° that was soluble in alcohol, acetone and in sodium bicarbonate solution.

5.089 mg sub.: 12.981 mg CO_2; 5.364 mg H_2O. Found %: C 69.57; H 11.79. $C_{15}H_{30}O_3$. Calculated %: C 69.70; H 11.70.

Benzylethyl Ester of Hexadecanoylmalonic Acid

48 g (0.2 mole) of the benzylethyl ester of malonic acid [7] in 75 ml of dry benzene was added to 4.6 g of metallic sodium (0.2g-atom) under a layer of 200 ml of dry benzene while the mixture was being stirred. After the sodium had completely reacted, 30 g of the acid chloride of palmitic acid (0.1 mole) was added in drops to the thickening reaction mass, and it was heated for half an hour on a water bath with a reflux condenser. The precipitate which formed was separated on a Büchner funnel, washed with benzene and after having been suspended in ether was decomposed with a 10% acid solution. The ethereal solution was dried with sodium sulfate and the ether driven off. The residue (53 g) consisted of the crude benzylethyl ester of hexadecanoylmalonic acid suitable for debenzylation and decarboxylation.

Ethyl Ester of β-Ketostearic Acid

30 g of the crude benzylethyl ester of hexadecanoylmalonic acid in 200 ml of anhydrous alcohol was hydrogenated in the presence of 5 g of palladinized barium carbonate (5% Pd). The hydrogenation slowed down after 1070 ml of hydrogen had been absorbed. After 10 g of palladinized barium carbonate had been added in three stages, 240 ml more of hydrogen was absorbed; a total of 1310 ml was absorbed (the theoretical quantity was 1460 ml). The catalyst was separated by filtration and the filtrate was heated to boiling for about an hour. After completion of the decarboxylation and distilling off the alcohol in a vacuum, the residue was vacuum distilled at 1.5 mm. The yield of the 135-175° fraction, which gave a sharp reaction with ferrous chloride for the presence of the keto group, was 13 g (60%).

After threefold vacuum redistillation, the β-ketostearic acid ester had a b p. of 162-172° at 1.5 mm, and solidified at a temperature below 15°.

3.799 mg sub.: 10.278 mg CO_2; 4.063 mg H_2O. Found %: C 73.83; H 11.97. $C_{20}H_{38}O_3$. Calculated %: C 73.57; H 11.73.

β-Hydroxystearic Acid

7 g of the ethyl ester of β-ketostearic acid was reduced in 200 ml of moist ether by 42 g of amalgamated aluminum shavings as in the preceding. The yield of the 144-147° (at 0.8 mm) fraction was around 3 g (43%).

3 g of the ethyl ester of β-hydroxystearic acid in 6 ml of alcohol was saponified with 12 ml of a 40% potassium hydroxide solution as in the preceding. The β-hydroxystearic acid had a m.p. of 86-87°. It consisted of thin white flakes (crystallized from petroleum ether). The yield was about 1 g.

2.278 mg sub.: 6.05 mg CO_2; 2.45 mg H_2O. Found %: C 72.47; H 12.03. $C_{18}H_{36}O_3$. Calculated %: C 71.93; H 12.08.

SUMMARY

1. The ethyl esters of β-ketotridecanoic and β-ketopentadecanoic acids were synthesized via the partial acidolysis of the acylmalonic esters obtained by the reaction of magnesiumethoxymalonic ester with the acid chlorides of undecanoic and tridecanoic acids.

2. The ethyl ester of β-ketooctadecanoic acid was obtained by the debenzylation of the benzylethyl ester of hexadecanoylmalonic acid in the presence of palladium on barium carbonate and by the decarboxylation of the monoethyl ester obtained.

3. The esters of the β-keto acids were converted into the esters of the corresponding β-hydroxy acids via reduction by aluminum amalgam in a medium of moist ether.

4. β-Hydroxy acids of the general formula $RCH(OH)CH_2COOH$, where $R = C_{10}H_{21}, C_{12}H_{25}, C_{15}H_{31}$ were obtained by saponification of their ethyl esters.

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CONDENSATION OF DIKETENE WITH CERTAIN ALIPHATIC KETONES

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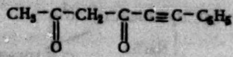
There are no data in the literature concerning the synthesis of acetylenic β-diketones. Taking into consideration the great reactivity of diketene in addition reactions, we undertook the synthesis of the acetylenic β-diketone – 1-phenylhexene-1-dione-3,5



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-C\equiv C-C_6H_5$$

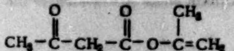
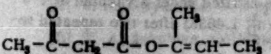
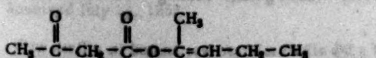
via the addition of phenylacetylene to diketene.

A number of our experiments in this field jointly with E. V. Kogan and K. A. Opaleva did not lead to positive results. In one of these experiments in which the reaction was carried out in acetone in the presence of pyridine, a liquid with a pleasant odor which gave characteristic reactions with ferrous chloride and bromine water, was obtained in place of the expected diketone. We assumed that this liquid consisted of the ester of acetoacetic acid and the enol form of acetone. We found no data in the literature concerning the reaction of diketene with ketones. On the contrary, in Boese's work [1], it was indicated that diketene does not react with ketones. However, this indication was found to be contrary to well-known data concerning the reaction of ketene (with which diketene is analogous in many of its properties) with ketones, with the formation of esters of acetic acid and the enol forms of the corresponding ketones [2].

On the strength of this the authors of the present work determined to investigate the reaction of diketene with certain aliphatic ketones – acetone, methylethyl ketone, and methylpropyl ketone – in greater detail.

Quite mobile, transparent, colorless liquids with a pleasant ethereal odor were obtained in all cases as a result of heating diketene with the indicated ketones in the presence of pyridine. The yield amounted to 50-55% of the theoretical, calculating on the basis of diketene. The constants of the substances obtained are given in the table.

TABLE

Formulas and designations of the substances obtained	B.p. (in °)	Pressure (in mm)	n_D^{28}	d_4^{28}	MR_D	
					Found	Calculated for the enol form
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{\mid}}{C}=CH_2$ α-Methylvinyl ester of acetoacetic acid (I)	77	4	1.4678	1.0769	37.52	36.77
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{\mid}}{C}=CH-CH_3$ sym. Dimethylvinyl ester of acetoacetic acid (II)	65	2	1.4696	1.0692	41.84	41.39
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{\mid}}{C}=CH-CH_2-CH_3$ sym. Methylethylvinyl ester of acetoacetic acid (III)	71-72	2	1.4702	1.0533	47.50	46.01

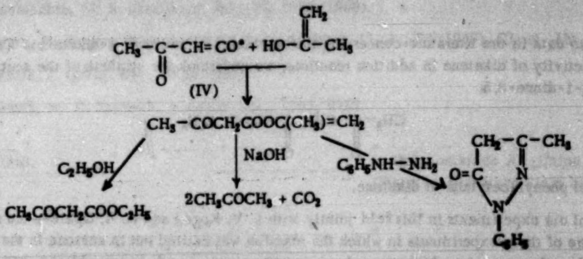
On the basis of the following facts we considered the products obtained to be ethers of acetic acid and enolic forms of the corresponding ketones formed by addition of the latter to diketene.

All the substances agreed in analytical data and molecular weight with the assumed empirical formulas (see substances (I), (II) and (III) in the table).

The ester (I) on heating with 5% alkali solution underwent saponification and ketone cleavage with evolution of approximately two moles of acetone per mole of ester.

On heating with absolute alcohol, the esters (I) and (II) underwent transesterification, forming acetoacetic ester with a 77% yield.

On heating with phenylhydrazine in the presence of absolute alcohol, (I) and (II) formed 1-phenyl-3-methyl-5-pyrazolone. The reaction of diketene (IV) with ketones proceeds according to the following scheme (for acetone):



The role of the catalyst – pyridine – in the condensation of diketene with ketones is evidently twofold. As a base it facilitates the enolization of ketones. On the other hand, pyridine, due to the presence of an incomplete electron pair at the nitrogen atom, activates diketene in the addition reaction (B. A. Porai-Koshits).

EXPERIMENTAL

The starting materials had the following characteristics:

diketene (98.5% pure) with a m.p. of 127.4° at 760 mm; 43° at 29 mm; d_4^{20} 1.0897; n_D^{20} 1.4379;**

acetone with a b.p. of 56-57°; d_4^{20} 0.792; n_D^{20} 1.3591;

methylethyl ketone with a b.p. 79-80°; d_4^{20} 0.805; n_D^{20} 1.3591;

methylpropyl ketone with a b.p. of 101-102°; d_4^{20} 0.810; n_D^{20} 1.3895.

The general procedure consisted of the following. A quantity of the ketone, usually five times as much volumetrically as the diketene, 0.5 ml of pyridine and 0.5 g of dry zinc sulfate were placed in a round-bottomed flask with a reflux water condenser. Diketene was slowly poured from a dropping funnel at room temperature. It was observed that some heat was evolved by the reaction mass and its temperature rose to approximately 28-30°, while the liquid became slightly yellow. The flask was shaken from time to time and then heated on a water bath for 4-6 hours. The conclusion of the reaction was determined by the disappearance of the diketene odor. The liquid became cherry red at the end of the reaction. The excess ketone was driven off in a column under a water jet pump and the residue was repeatedly fractionated under a vacuum at 2 or 4-5 mm.

I. Condensation of Diketene with Acetone

212 ml (3 moles) of acetone, 0.5 ml of pyridine, 0.5 g zinc sulfate and 39 ml (0.5 mole) of diketene were taken. After distilling off the acetone 53.6 g of substance was left which was redistilled under a vacuum at 3-4 mm. The chief fraction with a boiling point of 57-72° and amounting to 40 g (n_D^{22} 1.4635) after two repeated redistillations yielded 30.5 g of pure product with a b.p. of 77° at 4 mm, n_D^{20} 1.4678.

0.2522 g sub.: 0.5470 g CO_2; 0.1621 g H_2O. 0.1792 g sub.: 0.3846 g CO_2; 0.1124 g H_2O. Found %: C 59.19, 58.55; H 7.31, 7.02. $C_7H_{10}O_3$. Calculated %: C 59.15; H 7.09. 0.3944 g sub.: 30.26 g benzene: Δt 0.462°. Found: M 143.9. $C_7H_{10}O_3$. Calculated: M 142.

Hydrolysis and Cleavage. 4 ml of the ester with 1.5 ml of a 5% alkali solution was heated in a flask with a reflux condenser on a water bath for 6 hours. The contents of the flask were transferred to a flask with a fractionating column and 3.2 ml of acetone with a b.p. of 56-57° was distilled off. The yield was 73% of the theoretical.

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* Four possible structural formulas are ascribed to diketene, including that set forth.

** The authors are grateful to B.A. Porai-Koshits and M.S. Dinaburg for kindly furnishing the diketene.

Transesterification. 14.4 g of the ester and 10.2 g of absolute alcohol were heated in a flask with a reflux condenser on a water bath for 10-12 hours. The liquid obtained was fractionated twice, first under a water jet pump and then in a vacuum at 14-15 mm. 8.9 g of a substance with a b.p. of 69-71°, n_D^{20} 1.4219 was collected.. The product boiled at 180° at normal pressure. All of this agreed with the literature data for acetoacetic ester.

Preparation of 1-phenyl-3-methyl-5-pyrazolone. 5.4 g of phenylhydrazine (0.05 mole), 5 ml of absolute alcohol and 7.1 g (0.05 mole) of the substance were heated in a flask with a reflux water condenser and with a stirrer on a water bath for 6 hours. The reaction mass, poured into a glass and cooled, almost completely crystallized. The melting point of the raw product was 124° and was 126.5° for the recrystallized product. A mixed sample with pure phenylmethylpyrazolone yielded no depression. The yield of recrystallized product was 3.8 g.

II. Condensation of Diketene with Methylethyl ketone

50 ml of diketene, 175 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc sulfate were taken.

After distilling off the excess ketone and repeated redistillation, 11.3 g of product with a b.p. of 65° at 2 mm, n_D^{20} 1.4696 was obtained.

0.1419 g sub.: 0.3176 g CO_2; 0.1049 g H_2O. 0.2123 g sub.: 0.4765 g CO_2; 0.1476 g H_2O. Found %: C 61.08, 61.25; H 8.27, 7.78. $C_8H_{12}O_3$. Calculated %: C 61.52; H 7.75. 0.4193 g sub.: 31.29 g benzene: Δt 0.429°. Found: M 159.3. $C_8H_{12}O_3$. Calculated: M 156.

Transesterification. 4 ml of the ester and 5 ml of absolute alcohol were taken. 2.3 g of a substance with a b.p. of 50-52 att 4 mm was obtained; n_D^{20} 1.4232.

Preparation of Phenylmethylpyrazolone. 3 ml of the ester, 2 ml of phenylhydrazine and 0.5 ml of absolute alcohol were taken. 0.8 g of a product with a m.p. of 126° was obtained. A mixed sample gave no melting point depression.

III. Condensation of Diketene with Methylpropyl Ketone

20 ml of diketene, 92 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc sulfate were taken. 4.9 g of a product with a b.p. of 71-72° at 2 mm, n_D^{20} 1.4702 was obtained.

0.1597 g sub.: 0.3715 g CO_2; 0.1195 g H_2O. 0.1902 g sub.: 0.4411 g CO_2; 0.1433 g H_2O. Found %: C 63.42, 63.07; H 8.37, 8.43. $C_9H_{14}O_3$. Calculated %: C 63.52; H 8.29. 0.2592 g sub.: 32.19 g benzene: Δt 0.456°. Found: M 177.6. $C_9H_{14}O_3$. Calculated: M 170.2.

SUMMARY

1. The possibility of condensing diketene with aliphatic ketones – acetone, methylethyl ketone and methylpropyl ketone – was demonstrated.

2. It was demonstrated that the corresponding esters of the enol forms of the ketones and acetoacetic acid are formed at the same time, i.e., the *α*-methylvinyl, sym. dimethylvinyl and sym. methylethylvinyl esters.

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[1] A. B. Boese, Ind. Eng. Chem., 32, 16 (1940).

[2] B. H. Gwynn, Ed. F. Degaring, J. Am. Chem. Soc., 64, 2216 (1942).

[3] T. A. Sokolova, Collected works of the State Institute of Applied Chemistry, 38, 129 (1947); V. D. Lyashenko, T. A. Sokolova, J. Gen. Chem., 17, 1869 (1947).

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Transesterification. 14.4 g of the ester and 10.2 g of absolute alcohol were heated in a flask with a reflux condenser on a water bath for 10-12 hours. The liquid obtained was distilled. [illegible] boiled at 180° at normal pressure. All of this agreed with the literature data for acetoacetic ester.

Preparation of 1-Phenyl-3-Methyl-5-Pyrazolone. 5.4 g of phenylhydrazine (0.05 moles), 8 ml of absolute alcohol and 7.1 g (0.05 moles) of the [illegible] were heated in a flask with a reflux condenser [illegible] on a water bath for 6 hours. The reaction mass, poured into a glass and cooled, almost completely crystallized. The melting point of the raw product was 124° and was 126.5° for the recrystallized product. A mixed sample with pure phenylmethylpyrazolone yielded no depression. The yield of recrystallized product was 8.2 g.

II. Condensation of Diketene with Methylethyl Ketone

10 ml of diketene, 175 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc chloride were taken.

After distilling off the excess ketone and [illegible] 11.5 g of product with a b.p. of 85° at 2 mm, n_D^{20} 1.4598 was obtained.

0.1418 g sub.: 0.3175 g CO_2, 0.1049 g H_2O. 0.0820 g sub.: [illegible] g CO_2, [illegible] g H_2O. Found %: C 61.06, 61.25; H 8.27, 7.98. $C_8H_{12}O_3$. Calculated %: C 61.53; H 7.74. 0.4160 g sub.: 37.36 g benzene: Δt 0.386°. Found: M 155.3. $C_8H_{12}O_3$. Calculated: M 156.

Transesterification. [illegible] g of the ester and 6 ml of absolute alcohol were taken. [illegible] g of [illegible] was obtained n_D^{20} 1.4[illegible]

Preparation of Phenylmethylpyrazolone. 2 ml of the ester, 2 ml of phenylhydrazine and 0.5 ml of absolute alcohol were taken. 0.8 g of a product with a m.p. of 126.5° was obtained. A mixed sample gave no melting point depression.

III. Condensation of Diketene with Methylpropyl Ketone

10 ml of diketene, 95 ml of the ketone, 0.5 ml of pyridine and 0.5 g of zinc chloride were taken. 10.5 g of a product with a b.p. of 72-75° at 2 mm, n_D^{20} 1.4592 was obtained.

0.1507 g sub.: 0.3718 g CO_2, 0.1250 g H_2O. 0.1252 g sub.: [illegible] g CO_2, 0.1081 g H_2O. Found %: C 63.43, 63.57; H 9.27, 9.48. $C_9H_{14}O_3$. Calculated %: C 63.50; H 8.29. 0.2235 g sub.: [illegible] g benzene: Δt 0.450°. Found: M 177.8. $C_9H_{14}O_3$. Calculated: M 170.2.

SUMMARY

1. The possibility of condensing diketene with aliphatic ketones – acetone, methylethyl ketone and methylpropyl ketone – was demonstrated.

2. It was demonstrated that the corresponding esters of the enol form of the ketone and acetoacetic acid are formed at the same time, [illegible]

LITERATURE CITED

[1] A. B. Boese, Ind. Eng. Chem., 32, 16 (1940).

[2] [illegible], J. Am. Chem. Soc. 66, [illegible] (1944).

[3] T. A. Sokolova, Collected works of the First Institute of Applied Chemistry [illegible] 14 (1947); [illegible] Lyubomilov, T. A. Sokolova, J. Gen. Chem. 17, 1863 (1947).

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Department of Organic Chemistry

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* [illegible]

** [illegible] for kindly furnishing the [illegible]

MONOVINYLACETYLENE HOMOLOGS

III. CYCLIC DIENE ETHERS

I. A. Favorskaya and L. V. Fedorova

As we have previously shown [1], during the reaction of a cyclic enyne hydrocarbon – 1-acetylenyl-Δ'-cyclopentene with methyl alcohol in the presence of borium fluoride and mercuric oxide, the simultaneous addition of one, two, or three molecules of alcohol to the hydrocarbon occurs.

In the present work most attention has been paid to the study of cyclic diene ethers of the general formula $C_nH_{2n-5}OR$, which had not previously been studied in any way.

Diene ethers were prepared for the first time by A. A. Petrov by the dehalogenation of the ethers of saturated and unsaturated hydrohalides [2, 3]. Particular interest attached to the synthesis of diene ethers derived from monovinylacetylene. A. E. Favorsky and his students showed in a number of examples that in the presence of KOH under pressure the formation of various substituted ethers proceeds and in particular the formation of β-substituted ethers [4,5].

Klebansky and Chevychalova prepared acyloxy- and alkoxy derivatives of butadiene in the presence of mercuric oxide and boron fluoride [6, 7].

The introduction of an alkoxy group into the β-position of a diene system should increase its reactivity in the diene synthesis. Cyclic diene ethers, therefore, represent a suitable way to proceed via the diene synthesis on the one hand to various derivatives of bicyclic ketones of the decalone and hexahydroindanone series, and on the other hand, by reaction with quinone, to the little studied class of polycyclenediones and polycyclenetriones.

In discussing our results it is in the first place necessary to dwell on the synthesis of the initial cyclic enyne hydrocarbons. As was already indicated in the preceding article [1], the dehydration of acetylenic alcohols can be accompanied by a number of side reactions. 1-Acetylenyl-Δ'-cyclohexene was obtained by the dehydration of 1-acetylenylcyclohexanol-1 under various conditions.

In the last few years (1948-1952) indications have appeared in the literature to the effect that ethylbenzene [8, 9] is often contained in the dehydration products of 1-acetylenylcyclohexanol-1. However, no indications concerning the quantity of ethylbenzene as a function of the method of dehydration have been published.

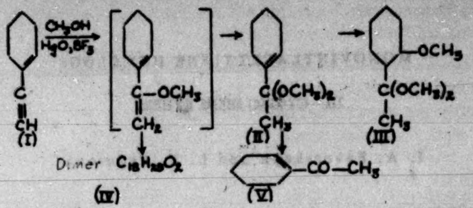
Our investigations showed that during catalytic dehydration over unfired porcelain and aluminum phosphate, the hydrocarbon obtained contains up to 80% in the first case and up to 20% in the second, of nonacetylenic hydrocarbon which did not add methyl alcohol in the presence of BF_3 and HgO (experiments 1-5, Table 1). The hydrocarbon recovered from the experiments did not yield a precipitate with an ammoniacal solution of cuprous oxide. It was established by spectroscopic investigation of it that it had the characteristic spectrum of ethylbenzene [10] (λ_{max} 2600 and 2650 A). The isolated hydrocarbon was prepared by the action of phosphorus oxychloride in pyridine on carbinol [11].

We recorded analogous data previously during the dehydration of 1-acetylenylcyclopentanol-1. The isomerization of 1-acetylenyl-Δ'-cyclopentene in methylfulvene was presented in detail in the previous article [1]. In the present investigation, 1-acetylenyl-Δ'-cyclopentene was also prepared by the reaction of carbinol with phosphorus oxychloride in pyridine and did not contain methylfulvene.

The reaction of the hydrocarbons obtained with methyl alcohol in the presence of HgO and BF_3 was studied further and cyclic diene ethers were prepared.

The addition of methyl alcohol to 1-acetylenyl-Δ'-cyclohexene proceeded somewhat differently than to 1-acetylenyl-Δ'-cyclopentene (see the preceding article) with regard to the ratios of the reaction products obtained

The addition of methyl alcohol to 1-acetylenyl-Δ'-cyclohexene can be represented by the following scheme:

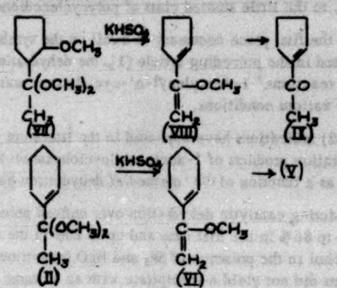


The following products were obtained as a result of the reaction: the dimethylketal of 1-acetyl-Δ'-cyclohexene (II) – 55%, the dimethylketal of 2-methoxy-1-acetylcyclohexane (III) – 3% and the dimer $C_{18}H_{28}O_2$ (IV) – 10%. The chief reaction product was the unsaturated ketal (II). The quantity of dimer was considerably less than in the case of the addition of alcohol to 1-acetylenyl-Δ'-cyclopentene. In view of the fact that the dimer (IV) and the methoxyketal (III) were obtained in insignificant quantities, they were not investigated in the present work.

The structure of product (II) was demonstrated by its hydrolysis in acid medium. The unsaturated ketone (V) was identified by comparison of its semicarbazone with the semicarbazone of 1-acetyl-Δ'-cyclohexene, obtained by hydration of 1-acetylenyl-Δ'-cyclohexene.

Since 1-acetyl-Δ'-cyclohexene (V) was the standard for the demonstration of the structure of the unsaturated ketal and diene monoether of 1-α-methoxyvinyl-Δ'-cyclohexene (VI), the ultraviolet absorption curve of its semicarbazone was taken; the curve completely coincided with the absorption curve of the semicarbazone of the acetylcyclohexene obtained by the reaction of carbinol with formic acid [12, 20].

The cyclic diene ethers: 1-α-methoxyvinyl-Δ'-cyclohexene (VI) and 1-α-methoxyvinyl-Δ'-cyclopentene (VIII) were prepared by splitting off methyl alcohol from the corresponding ketals and methoxyketals by redistillation over small quantities of potassium bisulfate.

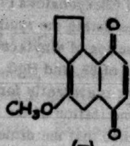


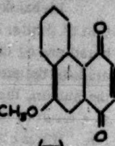
The structure of the diene ethers (VI) and (VIII) obtained was demonstrated by hydrolysis in the presence of dilute hydrochloric acid into the corresponding α,β-unsaturated ketones (V and IX).

The unsaturated ketones were identified via comparison of their semicarbazones with the semicarbazones of 1-acetyl-Δ'-cyclopentene and 1-acetyl-Δ'-cyclohexene obtained by hydration by Kucherov's method of the corresponding enyne hydrocarbons.

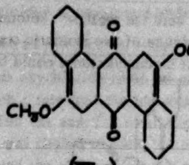
The structure of the cyclic diene ethers obtained was also confirmed by diene condensation with quinones. During the addition of 1-α-methoxyvinyl-Δ'-cyclopentene to p-benzoquinone at room temperature even after a few minutes after the addition of the quinone, the formation of the addition product (1,2-cyclopentano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8) (X) was observed. The reaction was completed in the course of 1 hour. It was possible to stop the reaction at the stage of addition of one molecule of the diene to the dienophile only by quick addition of the quinone to the diene.

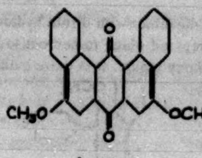
In the case of 1-α-methoxyvinyl-Δ'-cyclohexene, the formation of the addition product (1,2-cyclohexano-3-methoxy-1,4,910-tetrahydronaphthadione-5,8) (XI) was observed only after several hours. To wholly complete the reaction it was necessary to leave the reaction mixture overnight.


(X)


(XI)

By the use of a large excess of the diene (VI) and slow addition of the quinone to the reaction mixture,it was possible to obtain as the unique reaction product the product of the addition of two molecules of the diene to quinone with a yield up to 30-50% (XII-a or XII-b):

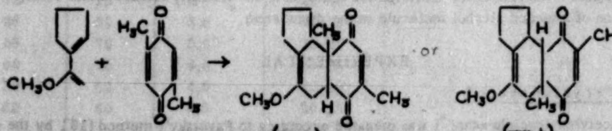

(XII-a)


(XII-b)

The given case appears to be an almost unique example of the preparation of a double addition product at room temperature. The addition of two molecules of the diene to the quinone at room temperature was observed in addition to this example only for cyclopentadiene.

1-Vinyl-Δ'-cyclohexene forms a double addition product with quinone only upon boiling in tetralin with a yield of 10% [13]. By analogy with the double addition product of 1-vinyl-Δ'-cyclohexene,the addition product of two molecules of 1-α-methoxyvinyl-Δ'-cyclohexene (VI) to quinone probably has the formula (XII-a) (9,10-diketo-3,7-dimethoxyoctahydro-1,2,5,6-dibenzanthracene). It is evident on the basis of the facts set forth that 1-α-methoxyvinyl-Δ'-cyclohexene is more reactivein the diene synthesis than 1-vinyl-Δ'-cyclohexene.

The addition of 1-α-methoxyvinyl-Δ'-cyclohexene to p-xyloquinone led to the preparation of a tricyclic methoxydiketone with an angular methyl group



(XIII-a) (XIII-b)

As regards a choice between formulas a and b, the structure of the compound obtained could not be determined in the present investigation.

With the object of demonstrating the structure of the compound (XIII) as a tricyclic α,β-unsaturated diketone with an angular methyl group, we took the ultraviolet spectrum of this compound (Fig. 1). These data coincided with the results obtained by Butz for a number of polycyclic diketone derivatives of 2-cyclohexene-1,4-dione [14].

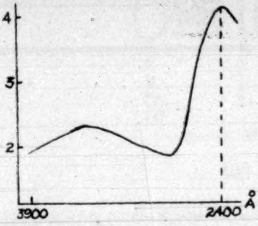


Fig. 1. Absorption curve of the tricyclic diketone with an angular methyl group. The solvent was ethyl alcohol, with 0.00002-0.00092 mole/liter λ_{max} = 2400A and ϵ = 10 120.

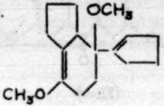
It had previously been noted by us [1] that the basic reaction product during the addition of methyl alcohol to 1-acetylenyl-Δ'-cyclopentene was the dimer of a diene monoether. In the present work its structure was more exactly established.

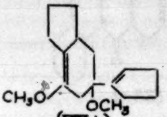
Klebansky and Chevychalova [7] gave indications of the formation of similar dimers during the synthesis of formoxy- and acetoxybutadiene by the reaction of vinylacetylene with the corresponding acids in the presence of BF_3 and HgO. In accord with the opinion of the authors, the dimer is evidently formed in the distillation process as a result of the dimerization of the monomer at an increased temperature. It was established that the dimers are cyclohexane derivatives.

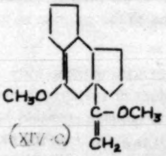
Nazarov [15] studied the thermal dimerization of formoxy- and methoxybutadienes and determined the structure of the dimers obtained as that of p-substituted methoxy- and formoxyvinylcyclohexenes. [See below.]

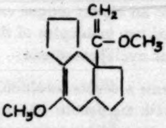
It can be assumed by analogy with these works that the structures (XIV-a, b, c, and d) are possible for the dimer obtained by us.

During the hydrolysis of the dimer with dilute hydrochloric acid the methoxy ketone $C_{15}H_{22}O_2$ was isolated, for which a semicarbazone was prepared which turned out to be a mixture of two isomeric semicarbazones. Both semicarbazones contained the methoxy group. It is quite evident that methoxyketones could be obtained only from the compounds (XIV-a) and XIV-b).


(XIV-a)


(XIV-b)


(XIV-c)


(XIV-d)

We tried to give another explanation of the formation of dimers of the diene ethers under the conditions of the addition reaction. It seemed more probable to us that dimerization proceeds in the instant of reaction under the influence of the catalyst BF_3 and HgO. With this object, analytically pure 1-α-methoxyvinyl-Δ'-cyclopentene was placed in contact with one drop of catalyst. A dimer analogous to the dimer (XIV) was obtained as a result. It is, consequently, quite evident that the dimer is formed not as a result of thermal dimerization, but as a result of the dimerization of the initially formed monoether under the influence of the catalyst. We consider that the yield of dimer during the addition reaction of alcohols to the vinylacetylenic hydrocarbons depends on the rates of two concurrent reactions – the rate of the dimerization reaction of the initially formed diene ether, and the rate of the addition reaction of a second alcohol molecule to the diene ether.

EXPERIMENTAL

1-Acetylenyl-Δ'-cyclohexene*

The initial 1-acetylenylcyclohexanol-1 was prepared according to Favorsky's method [16], by the condensation of cyclohexanone with acetylene in the presence of powdered potassium hydroxide. The yield of carbinol was 90%. B.p. 175-178°; m.p. 30-31° [17, 18].

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* In the present article, we considered it more convenient to change the nomenclature of the compounds previously obtained, which were described in the preceding communication, and considered all the compounds as derivatives of cyclopentane and cyclohexane – for example, in place of Δ'-cyclopentenylacetylene – 1-acetylenyl-Δ'-cyclopentene; in place of 2,2-dimethoxy-2-Δ'-cyclopentenylethane – dimethylketal-1-acetyl-Δ'-cyclopentene.

Dehydration of 1-Acetylenylcyclohexanol-1

a) Over unfired porcelain. 45 g of the carbinol was passed in a stream of CO_2 through a glass tube filled with unfired porcelain. The temperature of the dehydration was 240-250°. The duration of the dehydration was 6 hours. The dehydration product was collected in a receiving flask, which was cooled with snow. The yield was 40%.

B.p. 47-49° at 20 mm; n_D^{16} 1.4970.

The hydrocarbon was a mobile, colorless liquid which yielded a characteristic precipitate with Ilosvay reagent and with an ammoniacal silver oxide solution.

b) Over aluminum phosphate. The catalyst was prepared by Ogloblin's method [19]. 20 g of aluminum pohsphate obtained in this manner was stirred with 200 g of finely ground porous plates. Immediately before the dehydration, the catalyst was dried in a vacuum at 280-300°.

60 g of the carbinol was distilled for 3 hours in a nitrogen atmosphere through a glass tube filled with catalyst. The dehydration was carried out at 200 mm and 260-280°. The reaction product was collected in a receiving flask, cooled with a salt-snow mixture. The yield was 38.5%.

B.p. 76° at 100 mm; b.p. 47-49° at 20 mm; n_D^{16} 1.4975.

The hydrocarbon yielded a precipitate with an ammoniacal solution of silver oxide.

Preparation of 1-Acetylenyl-Δ'-cyclohexene

65 ml of phosphorus oxychloride in 65 ml of pyridine was added to 125 g of 1-acetylenylcyclohexanol-1 in 180 ml of pyridine at such a rate that the temperature was kept in a range of 105-110°. The reaction mass was energetically stirred. After the addition of all the phosphorus oxychloride the mixture was heated on a water bath for 1 hour, after which it was cooled to room temperature and poured out on ice. The pyridine was bound with 700 ml of 20% sulfuric acid and the hydrocarbon was extracted with ether. The ethereal solution was carefully washed with a solution of soda and dried with potash. The yield of hydrocarbon was 86%.

B.p. 74-75° at 90 mm; n_D^{20} 1.4956.

The hydrocarbon yielded the characteristic reactions for acetylenic hydrogen.

Addition of Methyl Alcohol to 1-Acetylenyl-Δ'-cyclohexene

The addition of methyl alcohol to 1-acetylenyl-Δ'-cyclohexene was carried out under the same conditions as the addition of methyl alcohol to 1-acetylenyl-Δ'-cyclopentene [1].

The conditions of the separate experiments and the yields of the products obtained are set forth in Table 1.

TABLE 1

Expt. No.	Quantity of reagents		Duration of the reaction (in hours)	Reaction temperature (in °)	Yield (in %)			Hydrocarbon recovered from the experiment (in g)
	hydrocarbon (in g)	alcohol (in g)			of the dimethoxy derivative	of the trimethoxy derivative	of the dimer	
1	15	25	2	22-24	8	–	–	12
2	26	30	3.5	22-23	38	4.2	8	7
3	58	70	5.0	22-25	42.6	4	5.7	12
4	60	75	4.5	20-25	48.8	4.8	10	13
5	50	60	4.5	20-25	44.5	4.3	10.4	10
6	62	80	4.5	20-25	55.5	2.7	11	–

In the first experiment hydrocarbon was taken for the reaction which had been obtained by the dehydration of 1-acetylenylcyclohexanol-1 over unfired porcelain; in experiments 2-5, hydrocarbon obtained by dehydration over aluminum phosphate was taken; in experiment 6 – hydrocarbon obtained by dehydration with phosphorus oxychloride was taken.

The hydrocarbon recovered had constants close to those of the initial 1-acetylenyl-Δ'-cyclohexene. Spectroscopic investigation of it showed that it had the characteristic spectrum of ethylbenzene.

Investigation of the Addition Product of Two Molecules of Alcohol to 1-Acetylenyl-Δ'-cyclohexene

B.p. 91° at 17 mm; 56° at 2 mm; d_4^0 0.9712; d_4^{20} 0.9542; n_D^{20} 1.4618; MR_D 49.03; calculated 49.00.

0.1363 g sub.: 0.3563 g CO_2; 0.1348 g H_2O; 0.0585 g sub.: 0.1514 g CO_2; 0.0577 g H_2O. 0.1849 g sub.: 17.0 g C_6H_6: Δt 33°. 0.1315 g sub.: 15.2 g C_6H_6: Δt 26°. 25.5 mg sub.: 17.7 ml 0.1 N $Na_2S_2O_3$. 25.4 mg sub.: 18.0 ml 0.1 N $Na_2S_2O_3$. Found %: C 70.73, 70.58; H 11.06, 11.06; M 170.73, 172.38; OCH_3 36.04, 36.61. $C_{10}H_{18}O_2$. Calculated %: C 70.54; H 10.66; M 170.24; OCH_3 36.46.

Hydrolysis of the Addition Product (II). 2 g of the substance (b.p. 55-56° at 2 mm and n_D^{20} 1.4617) was shaken in a test tube for several minutes with 6 ml of water and several (3-4) drops of hydrochloric acid. The hydrolysis product was salted out with potash and extracted with ether.

B.p. 89° at 18 mm; n_D^{16} 1.4907. The semicarbazone had a m.p. of 218-220°.

The data obtained corresponded with the literature data for 1-acetyl-Δ'-cyclohexene [12].

A mixed sample of the semicarbazone with a m.p. of 218-220° with the semicarbazone of known 1-acetyl-Δ'-cyclohexene displayed no melting point depression.

Preparation of 1-Acetyl-Δ'-cyclohexene. 0.3 g of mercuric sulfate and 45 ml of 70% aqueous methyl alcohol were placed in a flask supplied with a stirrer, a thermometer and a reflux condenser. The reaction mixture was energetically stirred and heated to 60° after which 9 g of 1-acetylenyl-Δ'-cyclohexene was added to it. The heating was continued for 2 hours in the course of which the temperature was held in the range 70-75° Upon completion of the heating, the reaction product was cooled to room temperature and poured out into a mixture of an aqueous solution of salt and ether. The ethereal solution was dried with potash. The yield of ketone was 8 g.

B.p. 84° at 16 mm; d_4^0 0.9852; d_4^{20} 0.9692; n_D^{20} 1.4904; MR_D 37.0; calculated 36.28. The semicarbazone had a m.p. of 220-221° (from alcohol).

The ultraviolet absorption curve (Fig. 2) of the semicarbazone of 1-acetyl-Δ'-cyclohexene was taken.

Preparation of the Diene Ether — 1-α-Methoxyvinyl-Δ'-cyclohexene (VI)

The splitting off of methyl alcohol from the unsaturated ketal (II) was carried out via vacuum distillation at 120 mm over potassium bisulfate, which had been preliminarily heated to 200-202° and finely ground.

0.15 g of potassium bisulfate and around 10 g of the ketal (II) were placed in a flask with a branched fractionating column and two tubes and the reaction mixture was heated on Wood's metal to 130°; at this temperature, splitting off of the alcohol began. As soon as the temperature became constant, 10 g of the ketal was gradually added from a dropping funnel into the flask at the same rate as the diene monoether which was being formed distilled off. The reaction was carried out in a stream of dry nitrogen at 120 mm. After a single redistillation, a fraction was isolated which agreed in properties with the diene ether.

B.p. 44.5-45° at 1 mm; b.p. 123° at 95 mm; d_4^0 0.9638; d_4^{14} 0.9556; n_D^{14} 1.5095; MR_D 43.21; calculated 42.27.

0.0872 g sub.: 0.2479 g CO_2; 0.0787 g H_2O. 0.0909 g sub.: 0.2598 g CO_2; 0.0825 g H_2O. 26.5 mg sub.: 11.6 ml 0.1 N $Na_2S_2O_3$; 32.2 mg sub.: 14.7 ml 0.1 N $Na_2S_2O_3$. 0.1285 g sub.: 13.36 g C_6H_6: Δt 0.39°. 0.0835 g sub.: 19.55 g C_6H_6: Δt 0.16°. Found %: C 77.54, 77.94; H 10.09, 10.15; OCH_3 22.63, 22.44; M 138.1, 138.2. $C_9H_{14}O$. Calculated %: C 78.33; H 10.22; OCH_3 22.44; M 138.2.

Hydrolysis of the Diene Monoether (VI). 2.0 g of the substance was shaken in a test tube with 4 ml of 3% hydrochloric acid. The hydrolysis products were neutralized with potash and extracted with ether.

B.p. 85° at 14 mm, n_D^{17} 1.4900. The semicarbazone melted at 218°.

A mixed sample with known semicarbazone of 1-acetyl-Δ'-cyclohexene displayed no melting point depression.

Preparation of 1-Acetylenyl-Δ'-cyclopentene

The experiment was carried out under the conditions described above for 1-acetylenyl-Δ'-cyclohexene from 1-acetylenylcyclopentanol-1 with phosphorus oxychloride in pyridine. The yield of hydrocarbon was 75%.

B.p. 57-59° at 100 mm; n_D^{18} 1.4900.

The hydrocarbon was a colorless liquid with the characteristic odor of acetylenic hydrocarbons and gave a precipitate with an ammoniacal solution of silver oxide and Ilosvay's reagent.

Preparation of the Diene Monoether 1-α-Methoxyvinyl-Δ'-cyclopentene (VIII)

The splitting off of methyl alcohol from the methoxyketal (VII) was carried out by the method already described for the preparation of 1-α-methoxyvinyl-Δ'-cyclohexene (VI). It should be noted that it is not recommended that a large quantity of (VII) be taken for the cleavage reaction, since prolonged heating of the reaction products in the presence of potassium bisulfate can lead to dimer formation.

The diene ether (VII) was a transparent liquid, which rapidly was polymerized in air.

B.p. 78° at 35 mm; n_D^{20} 1.4942; d_4^0 0.9491; d_4^{20} 0.9316; MR_D 38.82; calculated 37.65.

0.0870 g sub.: 0.2448 g CO_2; 0.0744 g H_2O, 0.0910 g sub.: 0.2555 g CO_2; 0.0795 g H_2O. 25.00 mg sub.: 12.2 ml 0.1 N $Na_2S_2O_3$. 0.1717 g sub.: 21.15 g C_6H_6: Δt 0.33°: 0.1315 g sub.: 13.96 g C_6H_6: Δt 0.40°. Found %: C 76.57, 76.74; H 9.67, 9.77; OCH_3 25.22; M 128.0, 124.2. Calculated %: C 77.40; H 9.65; OCH_3 25.00; M 124.17.

The lowered percentage of carbon in the analyses of the diene ether should be noted. In spite of repeated redistillation, we did not succeed in isolating fractions with a higher index of refraction. As has already been indicated, the diene ether is very rapidly polymerized in air and apparently absorbs oxygen, which is probably responsible for some discrepancy in the analyses.

Hydrolysis of the Diene Ether (VIII). 3.5 g of the substance and 5 ml of 3% hydrochloric acid were shaken in a test tube for 15-20 minutes, whereupon an appreciable evolution of heat in the reaction mixture was observed. The reaction products were neutralized with soda, extracted with ether and dried with potash. 2.5 g of the ketone was obtained.

B.p. 55-56° at 8 mm; n_D^{16} 1.4815. The semicarbazone had a m.p. of 207-208° (from alcohol).

1-Acetyl-Δ'-cyclopentene (IX), obtained by the hydration of 1-acetylenyl-Δ'-cyclopentene had:

b.p. 61-61.5° at 12 mm; n_D^{16} 1.4824 [1].

A mixed sample of the semicarbazone of the hydrolysis product and the semicarbazone of the known ketone displayed no melting point depression.

The ultraviolet absorption curve of the semicarbazone of the ketone was taken (Fig. 3) [20].

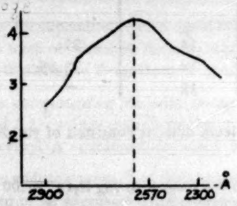

Fig. 2. Absorption curve of the semicarbazone of 1-acetyl-Δ'-cyclohexene. The solvent was ethyl alcohol; with 0.00113-0.00010 mole/liter, λ_{max} = 2570 A, ϵ = 23 200.

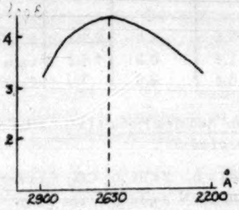

Fig. 3. Absorption curve of the semicarbazone of 1-acetyl-Δ'-cyclopentene. The solvent was ethyl alcohol; with 0.00305-0.000031 mole/liter, λ_{max} = 2630 A, ϵ = 25 300.

Addition of 1-α-Methoxyvinyl-Δ'-cyclopentene to p-Benzoquinone

1 g of twice sublimed p-benzoquinone was added to 2.5 g of the diene ether (VIII) (n_D^{20} 1.4900) dissolved in 20 ml of methyl alcohol, in the course of 5 minutes while the mixture was energetically stirred (ratio of diene and dienophile 2:1). Evolution of the addition product began immediately after addition of the quinone. The reaction was completed in the course of 1 hour.

The bulk of the addition product (X) contained an insignificant admixture of double addition product. After two recrystallizations from a mixture of petroleum ether with benzene (5:1), the mono- addition product consisted of shiny, orange flakes with a m.p. of 102-103°.

9.6 mg sub.: 25.52 mg CO_2; 5.94 mg H_2O; 9.16 mg sub.: 24.42 mg CO_2; 5.86 mg H_2O. 22.8 mg sub.: 5.9 ml 0.1 N $Na_2S_2O_3$. 0.0830 g sub.: 16.81 g C_6H_6: Δt 0.11°. Found %: C 72.54, 72.75; H 6.92, 7.15; OCH_3 13.41; M 232.5. Calculated %: C 72.41; H 6.89; OCH_3 13.40; M 232.2.

Addition of 1-α-Methoxyvinyl-Δ'-cyclopentene to p-Xyloquinone

3 g of the diene ether in 30 ml of absolute benzene and 1 g of xyloquinone were heated in a sealed tube on a water bath for 14 hours. (The ratio of diene to dienophile was 3.3:1).

The mixture, which initially had a brown color, gradually acquired a bright yellow coloration. After eliminating the benzene in a vacuum, the residue entirely crystallized. The yield of the addition product (XIII) was 1.4 g (74%); the addition product recrystallized from petroleum ether consisted of shiny lemon-yellow flakes with a m.p. of 94°.

7.23 mg sub.: 19.65 mg CO_2; 4.89 mg H_2O. 7.93 mg sub.: 21.50 mg CO_2; 5.37 mg H_2O. 55.0 mg sub.: 12.7 ml 0.1 N $Na_2S_2O_3$. 48 mg sub.: 11.0 ml 0.1 N $Na_2S_2O_3$. 0.0985 g sub.: 15.41 g C_6H_6: Δt 0.13°. 0.1020 g sub.: 16.64 g C_6H_6: Δt 0.125°. Found %: C 74.12, 73.94; H 7.70, 7.57; OCH_3 11.9, 11.9; M 254.6, 254.0. Calculated %: C 73.85; H 7.69; OCH_3 11.9; M 260.32.

The ultraviolet absorption spectrum was taken for Compound (XIII) (see the theoretical part).

Addition of 1-α-Methoxyvinyl-Δ'-cyclohexene to p-Benzoquinone

Depending on the ratio of diene and quinone and on the rate of addition of the quinone to the diene ether in the reaction mixture, the ratio between nono- and double addition products is changed.

By slow addition of the quinone and a large excess of the diene ether, we succeeded in obtaining a double addition product as the only reaction product (experiment 3). On using benzene as the solvent, no double addition product at all was obtained (experiment 2).

TABLE 2

Expt. No.	Quantity of reagents (in g)		Ratio of diene to quinone	Solvent (in ml)	Duration of addition of the quinone (in minutes)	Duration of the reaction (in hours)	Yield (in %)	
	diene	quinone					of mono- addition product	of double addition product
1	3.5	1.5	2.3:1	CH_3OH (15)	120	14	27	28
2	1.4	0.3	4.6:1	C_6H_6 (15)	15	14	73.5%	–
3	3.5	0.5	7:1	CH_3OH (20)	120	12	–	30

Mono- Addition Product (XI). After recrystallization from petroleum ether it consisted of yellow needles with a m.p. of 86-87°.

9.0 mg sub.: 24.05 mg CO_2; 6.14 mg H_2O. 7.72 mg sub.: 20.56 mg CO_2; 5.28 mg H_2O. 21.00 mg sub.: 5.1 ml 0.1 N $Na_2S_2O_3$. 0.0964 g sub.: 17.5 g C_6H_6: Δt 0.115°. 0.0810 g sub.: 15.5 g C_6H_6: Δt 0.12°. Found %: C 72.88, 72.63; H 7.63, 7.66; OCH_3 12.47; M 248, 249.7. Calculated %: C 73.14; H 7.36; OCH_3 12.6; M 246.

Double Addition Product (XII). After recrystallization from a mixture of benzene and petroleum ether (3:1) it consisted of fine white needles with a m.p. of 186°.

9.65 mg sub.: 26.4 mg CO_2; 7.32 mg H_2O; 4.81 mg sub.: 13.25 mg CO_2; 3.66 mg H_2O. 26.54 mg sub.: 8.09 ml 0.1 N $Na_2S_2O_3$. 0.0744 g sub.: 14.42 g C_6H_6: Δt 0.07°. Found %: C 74.66, 74.71; H 8.48, 8.48; OCH_3 15.79; M 382. Calculated %: C 74.96; H 8.39; OCH_3 16.14; M 384.4.

Dimerization of the Diene Monoether of 1-α-Methoxyvinyl-Δ'-cyclopentene Under the Influence of HgO and $BF_3 \cdot (C_2H_5)_2O$

The catalyst was prepared in the same way as in the experiments involving the addition of methyl alcohol to hydrocarbon. 5 ml of anhydrous benzene and one drop of catalyst were placed in a reaction flask supplied with a stirrer and a dropping funnel; 3 g of analytically pure monoether (n_D^{20} 1.4942, % OCH_3 25.2) in a solution of 5 ml of anhydrous benzene was slowly added from a dropping funnel into the flask. The reaction mixture evolved heat vigorously and darkened. The reaction products were neutralized with finely ground potash (0.25 g), the residue filtered off, the benzene distilled off and the residue redistilled in a vacuum. 1.5 g of a substance with a b.p. of 145° at 2 mm was obtained which corresponded with the boiling point of the dimer $C_{16}H_{24}O_2$ (XIV).

The dimerization was carried out twice. 3.5 g of the dimer was obtained, which was then subjected to hydrolysis.

Hydrolysis. 3 g of the dimer was energetically shaken with 20 ml of 3% hydrochloric acid for 3 hours. The hydrolysis products were neutralized with soda, extracted with ether and dried with potash. 2.2 g of a ketone with a b.p. of 143-144° was obtained by distillation at 2.5 mm. The semicarbazone of the ketone was prepared which turned out to be a mixture of two isomeric semicarbazones. By fractional recrystallization from alcohol, the following were isolated:

1) a semicarbazone with a m.p. of 236-238°,

0.8020 g sub.: 10.45 ml N_2 (22°, 759 mm). 0.0560 g sub.: 7.2 ml N_2 (16°, 751 mm). 14.0 mg sub.: 2.75 ml 0.1 N $Na_2S_2O_3$. 23.8 mg sub.: 4.8 mg 0.1 N $Na_2S_2O_3$. Found %: N 14.82, 14.91; OCH_3 10.15, 10.58. Calculated %: N 14.47; OCH_3 10.65;

2) a semicarbazone with a m.p. of 220-222°.

0.0969 g sub.: 12.5 ml N_2 (20°, 758.6 mm). 0.1057 g sub.: 13.5 ml N_2 (24°, 764 mm). 22.8 mg sub.: 4.8 ml 0.1 N $Na_2S_2O_3$. 45.5 mg sub.: 9.4 ml 0.1 N $Na_2S_2O_3$. Found %: N 14.87, 14.60; OCH_3 10.90, 10.70. Calculated %: N 14.47; OCH_3 10.65.

Mixed samples with corresponding samples of semicarbazones obtained by hydrolysis of the dimer (XIV) displayed no melting point depression. Consequently, as a result of the hydrolysis of the dimer obtained during the low temperature dimerization of the diene ether 1-α-methoxyvinyl-Δ'-cyclopentene, a mixture of isomeric substituted hexahydroindanones is formed.

SUMMARY

1. It was shown that during the dehydration of 1-acetylenylcyclohexanol-1 over unfired porcelain and aluminum phosphate a hydrocarbon −1-acetylenyl-Δ'-cyclohexene− is formed which is isomerized into ethylbenzene.

2. The unsaturated dimethylketal 1-acetyl-Δ'-cyclohexene is formed as the chief reaction product by the action of methyl alcohol in the presence of $BF_3 \cdot (C_2H_5)_2O$ and HgO on 1-acetylenyl-Δ'-cyclohexene.

3. The corresponding cyclic diene ethers: 1-α-methoxyvinyl-Δ'-cyclohexene and 1-α-methoxyvinyl-Δ'-cyclopentene were obtained by the cleavage of methyl alcohol from the dimethylketal of 1-acetyl-Δ'-cyclohexene and the dimethylketal of 2-methoxy-1-acetylcyclopentane.

4. The corresponding tricyclic methoxydiketones: 1,2-cyclopentano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8 and 1,2-cyclohexano-3-methoxy-1,4,9,10-tetrahydronaphthadione-5,8 were obtained by the addition of 1-α-methoxyvinyl-Δ'-cyclopentene and 1-α-methoxyvinyl-Δ'-cyclohexene to p-benzoquinone.

5. The addition product of two molecules of diene to p-benzoquinone could be synthesized at room temperature by the use of an excess of the diene 1-α-methoxyvinyl-Δ'-cyclohexene.

6. A tricyclic methoxydiketone with an angular methyl group was obtained by the addition of 1-α-methoxyvinyl-Δ'-cyclopentene to p-xyloquinone.

7. The cyclic diene ethers obtained −1-α-methoxyvinyl-Δ'-cyclopentene and 1-α-methoxyvinyl-Δ'-cyclohexene− are reactive dienes and can be utilized for the synthesis of various polycyclic systems.

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CONDENSATION OF ANILINE WITH GLYCERIN, PARALDEHYDE AND ACETYLENE OVER ALUMINUM SILICATE

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It is mentioned in Chichibabin's communication [1] that lepidine, quinaldine and indole are formed by the passage over aluminum oxide of a mixture of acetylene and aniline vapors, with lepidine being formed in the largest quantity. Subsequently, Chichibabin and Oparina [2] carried out experiments involving the condensation of acetaldehyde and also of paraldehyde with aniline in the presence of aluminum oxide at 370-500°. The 220-270° fraction consisted of quinolinic bases and served for the preparation of the picrates of lepidine and quinaldine in a quantity of 28% of the first (experiments at 490-500°), and 6.5-10.4% of the second (experiments at 380-410°), calculating on the basis of the aniline which reacted. The authors expressed a hypothesis concerning the intermediate formation of crotonaldehyde, the presence of which they did not demonstrate experimentally [2].

The present investigation is devoted to elucidating the possibility of the direct synthesis of quinoline and also of quinaldine via the condensation of aniline with glycerin, paraldehyde and acetylene in the vapor phase over an aluminum silicate catalyst.

EXPERIMENTAL

The starting materials consisted of: 1) aniline with a b.p. of 183-184°; d_4^{20} 1.022, n_D^{20} 1.5863; 2) glycerin, dehydrated by heating to 180°; 3) paraldehyde with a b.p. of 124-125°, d_4^{20} 0.994; 4) acetylene, which was passed through a solution of potassium permanganate and chromic mixture before introduction into the reaction flask.

The experiments were conducted in an apparatus of the circulating type in a tube made of pyrex glass, in which aluminum silicate in the form of grains 2 mm in diameter was placed. A preliminary preheating was carried out in the upper part of the tube filled with glass rings. The aluminum silicate was replaced after each experiment. The fresh catalyst was activated by blowing air through it at 490-500° (4 hours). After each experiment, the catalyst was regenerated by blowing air at 500° for 2-3 hours through it until CO_2 was completely absent in the outgoing gas. The material balance of the experiments was arrived at according to the weight of raw materials and of the liquid and gaseous reaction products formed. The coke, resin and loss were calculated by differences.

Condensation of Glycerin with Aniline

In various experiments, glycerin was passed over aluminum silicate for 1 hour at 380° at a rate of 1 volume per 1 volume of catalyst per hour and for 20 minutes at 450° at a rate of 3 volumes per 1 volume of catalyst per hour. The liquid reaction products had a sharp odor and consisted of an aqueous and an oily layer. The water layer was separated and subjected to analysis. The test for the formation of a silver mirror was positive; dimedone gave a derivative which, after recrystallization from alcohol, melted at 191° (according to the literature data [3], the melting point of acroleindimedone is 192°). Acrylic acid was produced by oxidation of the water layer with silver oxide. Found %: Ag 60.6, 60.3. Calculated %: Ag 60.1. The acrolein content, determined quantitatively by Ripper's method [5], turned out to be equal to 35.6% at 380° and 46.5% at 450°. The water content, determined by the carbide method [4], amounted respectively to 50 and 36%.

The gaseous reaction products chiefly consisted of hydrogen and carbon dioxide gas (see the table) which substantially differed from the gas obtained by Nef [6] by the pyrolysis of glycerin.

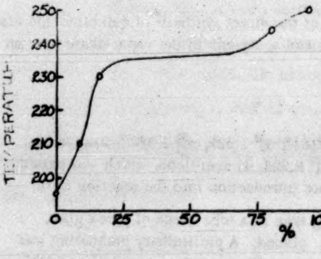
The yield (in percentage by weight) of acrolein at 380° amounted to 24% and at 450° to 26.2%, calculating on the basis of the glycerin passed through. Correspondingly, the yield of polymers was 7.9 and 12.3%, the yield of coke 19.3 and 20.2%, and the yield of water 33.9 and 20.3%. It is noteworthy that the portion of excess water in comparison with that which is formed by the dehydration of glycerin to acrolein amounts at 380° to 18.5% and at 450° to 3.5%. In view of the close yields of acrolein and coke and the twice greater yield of gas at 450°, it is necessary to assume that at 380° a considerable quantity of the acrolein which forms is converted into coke and polymers. At 450°, the basic sources for the formation of coke and polymers are the dehydration products of glycerin.

TABLE

Starting material	Experimental conditions			Gaseous reaction products (in volume %)				Yield of gas (in % by weight)
	Duration (in mins.)	Temp. (in °)	Volumetric rate	CO_2	H_2	C_nH_{2n}	C_nH_{2n+2}	
Glycerin	60	380	1:1	27.0	47.6	13.9	11.5	5.0
Glycerin	20	450	3:1	11.4	58.4	10.2	20.0	10.1
Glycerin + aniline	90	400	1:1	19.1	57.5	9.5	13.9	1.9
Aniline + paraldehyde	60	395	1:1	38.2	–	14.3	47.5	–
The same	60	400	1:1	43.4	–	16.2	40.4	–
Paraldehyde	30	370	1:1	41.0	–	50.0	9.0	12.6

After the experiments with glycerin, three experiments were carried out in which for an hour a mixture of aniline and glycerin (molar ratio 1:2) was passed over aluminum silicate at a temperature of 398-402° and a rate of 1 volume per 1 volume of catalyst per hour. The results of these experiments showed that on the average the yield (in % by weight) of aqueous layer amounted to 31.6%, of the oily products 49.9% and of coke 18.5%.

It was shown that increasing the duration of the experiment to an hour and a half did not change the results. In four experiments, a total of 150 g of the mixture was passed through and 122 g of liquid products was obtained.



Distillation curve.

The oily product (6.17 g) combined from the four experiments was rendered alkaline with sodium hydroxide and steam distilled. The base in the distillate separated in the form of an oily liquid; the aqueous part was extracted three times with ether. The oil was combined with the ethereal extract and the ethereal solution obtained was dried with solid alkali. The ether was distilled from the flask with a fractionating column, while the oily residue was distilled from a Würtz flask. The following fractions were taken off: 1st to 195°, 44.3 g (chiefly unreacted aniline); 2nd 195-210°, 1.23 g, n_D^{20} 1.5739, picrate m.p. 200.5°; 3rd 210-230°, 1.16 g, n_D^{20} 1.5971, picrate m.p. 201.5°; 4th 230-244°, 9.70 g, n_D^{20} 1.6251, M 128, picrate m.p. 202.0°, iodomethylate m.p. 132.5°; 5th 244-250°, 2.25 g, n_D^{20} 1.6271, picrate m.p. 201.0°. There was 0.69 g of residue in the flask.

Calculating on the basis of the total fraction boiling above 195°, the yield of the fourth fraction amounted to 64.5%, which amounted to 19.2% calculating on the basis of the aniline passed through.

The character of the distillation curve indicates that the bulk of the 230-244° fraction boils at a temperature close to the boiling point of quinoline. The molecular weight and index of refraction of this fraction are close to those for quinoline; the melting points of the picrate and iodomethylate obtained from the 230-244° fraction corresponded with those for quinoline.

The literature data for quinoline: b.p. 238° [7], 239° [10], 237° [11, 12], $n_D^{18.2}$ 1.6283 [13], picrate m.p. 203° [7, 10], iodomethylate m.p. 133° [10].

Condensation of Aniline with Paraldehyde

The conversion of paraldehyde over aluminum silicate was studied at 360-370° and a supply rate of 1 volume per 1 volume of catalyst per hour with an experimental duration of 25-35 minutes. The yield (average of three experiments in % by weight): 75.5% of liquid products, 12.8% of gaseous products, and 11.7% of coke (calculating on the basis of paraldehyde passed through). The quantity of unreacted acetaldehyde was 6.4%; the yield of the water-aldehyde portion of the catalyzate was 63.2%, and the yield of oily product was 5.9%. The water-aldehyde portion of the catalyzate was subjected to fractional distillation into the following fractions: 1st 20-50°, 2nd 50-75°, 3rd 75-90°, 4th 90-103°.

The dimedone derivative of the 1st fraction melted at 140°, which was in excellent agreement with acetaldehydedimedone. The dimedone derivative prepared from the 4th fraction melted at 182°, which corresponded to the melting point of the corresponding crotonaldehyde derivative. The literature data for crotonaldehyde are [3, 10]: b.p. 103°, melting point of the dimedone derivative 183°. The content of H_2O in the aqueous layer, determined by the carbide method, was 15%.

Thus, paraldehyde, under the influence of aluminum silicate, is depolymerized into acetaldehyde, which then condenses in the crotonic pattern.

The gaseous products consist primarily of unsaturated hydrocarbons and carbon dioxide gas (see the table).

The experiments involving the condensation of aniline with paraldehyde were carried out at 380-400°, the volumetric rate was 1 volume per 1 volume of catalyst per hour; the duration of the experiment was 1 hour; the molar ratio of aniline to paraldehyde was 1:0.66. The yield (average of five experiments) of liquid products amounted to 86.0% by weight, calculating on the basis of the mixture passed through. The portion of the oily part in the products obtained amounted to 66.5%, of the water-aldehyde part 19.5%, and of coke 14%.

The oily portion of the catalyzate was investigated by the method described above; it consisted of 74% of unreacted aniline and 26% of residue, which boiled above 195°. 7 g of nitrosocompound was obtained from 21 g of this residue, while the remaining portion was separated and fractionally distilled into the following fractions: 1st 195-210°, 2nd 210-223° and 3rd 223-250° (n_D^{20} 1.602, picrate m.p. 190°).

The yield of the 3rd fraction amounted to 14.8% by weight of the aniline passed through. The literature data for quinaldine [8, 10, 13]: b.p. 247°, n_D^{20} 1.607, picrate m.p. 191°.

The secondary amines obtained by reduction of the nitrosocompounds were fractionally distilled into the following fractions: 1st 195-200°, 2nd 200-214°, the 2nd fraction had n_D^{20} 1.5520; the picrate m.p. of 132°. The literature data [3, 10, 13] for ethylaniline: b.p. 204-205°; n_D^{20} 1.5559; picrate m.p. 132°.

Condensation of Aniline with Acetylene

In the condensation of aniline with acetylene the latter was introduced in a quantity approximately 2 times greater than that required according to the equation for the formation of quinaldine.

The experiments were carried out at 450°, the volumetric rate of aniline was 0.5 volumes per 1 volume of catalyst per hour and the duration of the experiment was 1 hour. The average yield of four experiments (in % by weight) of liquid products amounted to 95.8%, and of coke 4.2%, of the aniline passed through.

The catalyzate was analyzed as described above and yielded 26% of a residue which boiled above 195° and was further fractionally distilled into the following fractions: 1st 195-210°, 2nd 210-238°, 3rd 238-250°; the 3rd fraction had a n_D^{20} 1.602; picrate m.p. 187°. These values were close to those for quinaldine.

Another series of experiments was carried out at 450-460°; the volumetric rate of introduction of aniline was 0.4 volume per 1 volume of catalyst per hour; the acetylene was saturated with water vapor. The water was introduced into the reaction zone since the possibility of hydration of acetylene into acetaldehyde was assumed; further course of the reaction was according to the schemes described in the literature [9]. The yield (average of six experiments in % by weight) of liquid products amounted to 89% and 11% of coke based on the aniline passed through. The fractional distillation of the catalyzate showed that it amounted to 61% of unchanged aniline and to 26% of a residue which boiled above 195°. After diazotization of this residue and separation of the nitrosocompound, the following fractions were obtained: 1st 195-210°, 1.7%; 2nd 210-232°, 2.4%; 3rd 232-250°, 5% (of the aniline passed through); the 3rd fraction had a n_D^{20} 1.604, the picrate m.p. 189.5°, the iodomethylate a m.p. of 194°. These data agreed with the literature data for quinaldine.

The composition of the outgoing gas: acetylene 24%, hydrogen 12%, saturated hydrocarbons 64%.

SUMMARY

1. The possibility of direct synthesis of quinoline, quinaldine and ethylaniline by the condensation of aniline with glycerin paraldehyde and acetylene in the vapor phase over aluminum silicate was demonstrated in principle. The catalytic action of aluminum silicate in this synthesis turned out to be analogous to the action of aluminum oxide observed by Chichibabin and Oparina.

2. It was established that under the influence of aluminum silicate glycerin is dehydrated to acrolein, the maximum yield of which, under the conditions studied, reaches 43 mole % of the glycerin taken.

3. It was shown that condensation of aniline with glycerin or paraldehyde proceeds under the influence of aluminum silicate with the evolution of hydrogen and with the formation of acrolein or crotonaldehyde as intermediate products. Consequently, the mechanism of the condensation which proceeds under the influence of aluminum silicate is analogous to the mechanism of the synthesis of Skraup and Dobner-Miller.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

VIII. CONDENSATION OF 2-METHYLCYCLOHEXANOL AND 3-METHYLCYCLOPENTANOL WITH BENZENE

N. G. Sidorova

Being occupied with the study of the condensations of cyclic alcohols with benzene in the presence of aluminum chloride, we set ourselves the goal of elucidating the degree and direction of isomerization of cyclic radicals as a function of the reaction conditions in the case of the isomeric methylcyclohexanols and methylcyclopentanols.

The condensations of methylcyclohexanols [1] and methylcyclohexenes [2] with aromatic compounds in the presence of acid catalysts are usually accompanied by isomerization with migration of hydrogen. As a result of the reaction of all the initial cyclic compounds substances are formed in which the aryl group is found at the same carbon atom to which the methyl group is attached. The condensation of analogous cyclopentane compounds (with the exception of 1-methylcyclopentanol and 1-chloro-1-methylcyclopentane [3]) has not been studied at all.

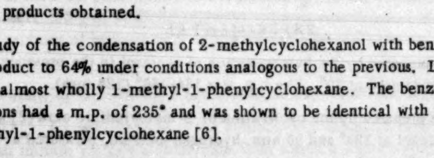
It seemed to us that the direction of the reaction in these condensations depends on the conditions and that under gentle conditions isomerization could be avoided. To verify this assumption, we studied the condensation of 2-methylcyclohexanol and 3-methylcyclopentanol with benzene under various conditions. In the case of 2-methylcyclohexanol, the isomerization should proceed particularly readily, since the methyl and hydroxyl groups are found on neighboring carbon atoms. The reaction with 2-methylcyclohexanol has already been studied by us together with Tsukervanik [4]. Under the conditions described, a product was obtained in a yield of 42.5% which, without special evidence, was taken to be 1-methyl-1-phenylcyclohexane.

The condensation of 1-chloro-2-methylcyclohexane with benzene in toluene in the presence of aluminum chloride has recently been described [5]. The author (also without evidence) ascribes the structure of 1-methyl-2-arylcyclohexanes to the products obtained.

In pursuing the study of the condensation of 2-methylcyclohexanol with benzene, we were able to increase the yield of reaction product to 64% under conditions analogous to the previous. Investigation of the reaction product showed that it was almost wholly 1-methyl-1-phenylcyclohexane. The benzamino derivative obtained from it after three crystallizations had a m.p. of 235° and was shown to be identical with the benzamino derivative of a known sample of 1-methyl-1-phenylcyclohexane [6].

However, even in the earlier work [4], it was qualitatively noted that in this reaction a little hydrocarbon is formed in which the phenyl group stands at the secondary carbon atom – evidently, 1-methyl-2-phenylcyclohexane. With the object of increasing the yield of this nonisomerized hydrocarbon, we carried out a number of condensations of 2-methylcyclohexanol with benzene under still more gentle conditions – during very slow addition of aluminum chloride and a very large excess of benzene (from 15 to 25 moles per 1 mole of alcohol).

The product obtained by the use of a 15-fold excess of benzene (yield 63% of the theoretical), was close in its constants to those of 1-methyl-1-phenylcyclohexane and the condensation product under severe conditions. The condensation product with the use of a 25-fold quantity of benzene (yield 73%) was appreciably different from them. Its dehydrogenation over platinum catalyst [7] yielded about 40% fluorene, approximately the same quantity of diphenyl, and some liquid hydrocarbon. The formation of these substances indicated that condensation under these conditions proceeds in two directions:

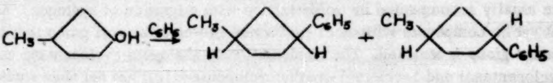


1-Methyl-2-phenylcyclohexane, evidently, is produced in the form of two stereoisomers.

Benzamino derivatives were obtained from the products of both the latter condensations which markedly differed from the benzamino derivatives of 1-methyl-1-phenylcyclohexane and the product of the first condensation, but they also differed among themselves. Both of these benzamino derivatives consisted of mixtures, and could not be entirely separated into the indidivual substances.

The condensations of 3-methylcyclopentanol with benzene were also carried out under various conditions. This reaction proceeds with considerably more difficulty than the analogous condensations of methylcyclohexanols and 1-methylcyclopentanol [3]. Only methylcyclopentene, chloromethylcyclopentane and the dimer of methylcyclopentene were formed with 0.7 g-equivalent of aluminum chloride. The reaction could be accomplished only with 0.9 g-equivalent of aluminum chloride and even in this case, a portion of the alcohol remained unreacted.

The condensation of 3-methylcyclopentanol with benzene both under gentle and under severe conditions yielded the same products —stereoisomeric 1-methyl-3-phenylcyclopentanes:



We did not succeed in even one case in demonstrating the presence of 1-methyl-1-phenylcyclopentane, although, possibly, it is formed in a large quantity.

The identification of the reaction products was achieved by the preparation of acetamino- and benzamino derivatives. Both of these derivatives were prepared in the form of mixtures. By fractional crystallization only one acetamino derivative and one benzamino derivative were isolated, evidently from the trans- form of the hydrocarbon.

Such a difference in the behavior of the methylcyclohexanols and methylcyclopentanols can be explained only by the fact that in the immobile five-membered ring, substituents are more rigidly bound.

EXPERIMENTAL

2-Methylcyclohexanol was prepared by the hydrogenation of o-cresol in the presence of Raney nickel at 180° and 120 atm. hydrogen pressure, measured at 20°. The b.p. was 164-166° (725 mm).

3-Methylcyclopentanol was prepared by the cyclization of β-methyladipic acid [8] and the hydrogenation of the ketone obtained over Raney nickel at 120° and 90 atm. hydrogen pressure, measured at 15°. The b.p. was 151-152°.

Condensation of 2-Methylcyclohexanol with Benzene Under Severe Conditions

In the reaction were taken: 2-methylcyclohexanol 11.4 g (0.1 mole), benzene 55 g (0.7 mole), $AlCl_3$ 9.2 g (0.07 mole). Aluminum chloride was added to the mixture of methylcyclohexanol with benzene, during constant shaking of the reaction mixture, in small portions for 1 hour. The reaction mixture was then heated initially on a warm, and then on a boiling water bath to cessation of the evolution of the bulk of hydrogen chloride. The isolation of the reaction product was carried out in the usual manner. 11.12 g (63.8%) of a hydrocarbon with a b.p. of 225-250° was obtained. After two-fold distillation over sodium 1-methyl-1-phenylcyclohexane was isolated:

b.p. 119-121° (17 mm); d_4^{20} 0.9372; n_D^{20} 1.5210; MR_D 56.58; calculated 56.43.

0.1002 g sub.: 0.3286 g CO_2; 0.0951 g H_2O. Found %: C 89.44; H 10.55. $C_{13}H_{18}$. Calculated %: C 89.65; H 10.35.

A benzamino derivative was obtained (by the usual method [9] without purification of the intermediate products) from the hydrocarbon, which had a m.p. of 223-230° prior to purification and even after three recrystallizations from alcohol melted at 235°.

5.05 mg sub.: 0.235 ml N_2 (725 mm, 25°). Found %: N 4.96. $C_{20}H_{23}ON$. Calculated %: N 4.78.

A mixture of it with the benzaminoderivative of 1-methyl-1-phenylcyclohexane (m.p. 235°) also melted at 235°.

Condensation of 2-Methylcyclohexanol with Benzene Under Mild Conditions

I. The following were taken in the reaction: 2-methylcyclohexanol 17.1 g (0.15 mole), benzene 175 g

(2.25 moles), $AlCl_3$ 14 g (0.105 mole). Aluminum chloride was added to the water-cooled mixture of benzene and 2-methylcyclohexanol in very small portions for 6 hours while the mixture was energetically stirred.

Each successive portion was added only after complete solution of the preceding. The mixture was then left for 5 days (slight evolution of HCl occurred), after which several drops of water were added to it and the reaction was completed by heating on a warm water bath (40-50°) for several hours to almost complete cessation of HCl evolution. The further treatment was as usual.

By distilling the reaction products 1.1 g of methylcyclohexyl chloride was obtained which redistilled at 90-100° (95 mm) and 16.5 g (63.2%) of a mixture of hydrocarbons with a b.p. of 125-127° (22 mm), which was purified by secondary distillation over sodium:

d_4^{20} 0.9355; n_D^{20} 1.5180; MR_D 56.41; calculated 56.43.

0.1045 g sub.: 0.3426 g CO_2; 0.0972 g H_2O. Found %: C 89.41; H 10.33. $C_{13}H_{18}$. Calculated %: C 89.65; H 10.35.

The benzamino derivative obtained from the alkylation product consisted of a mixture which was separated by fractional crystallization from alcohol and crystal sorting; two forms of crystals were thereby isolated – shiny needles and lusterless globules. The shiny crystals had a m.p. of 196-197°

5.16 mg sub.: 0.244 ml N_2 (29°, 723 mm). Found %: N 4.96. $C_{20}H_{23}ON$. Calculated %: N 4.78.

The lusterless crystals after isolation, melted at 170-175°. The results of their analysis agreed with those of the benzamino derivative of methylphenylcyclohexane.

7.85 mg sub.: 0.355 ml N_2 (19°, 722 mm). Found %: N 4.92. $C_{20}H_{23}ON$. Calculated %: N 4.78.

The melting point of this substance was increased by further crystallization and did not reach a definite limit. The crystal portion with the highest melting point melted at 196-202°.

II. The following were taken for the reaction: 2-methylcyclohexanol 15.6 g (0.137 mole), benzene 265 g (3.4 moles), $AlCl_3$ 12.8 g (0.095 mole).

The reaction was carried out analogously to the preceding, but the mixture was left for 7 days. By distillation of the reaction products, 2,5 g of methylcyclohexyl chloride was obtained which redistilled at 95-100° (100 mm) and 17.3 g (72.7%) of a mixture of hydrocarbons with a b.p. of 116-118° (14 mm). Secondary distillation over sodium yielded the product:

B.p. 113-114° (13 mm); d_4^{20} 0.9442; n_D^{20} 1.5249; MR_D 56.51; calculated 56.43.

Dehydrogenation [7]. A single passage of the hydrocarbons through a tube with platinized carbon at 300-320° at a rate of 2-3 drops per minute yielded a catalyzate from which a liquid hydrocarbon with a b.p. of 124-126° (15 mm); d_4^{20} 0.9979; n_D^{20} 1.5780, consisting of a mixture of unnamed hydrocarbons with the dehydrogenation product, was isolated by distillation. The residue after distillation was fluorene. The m.p. was 115°; the picrate melted at 79°. The yield was around 10%. Repeated passage of the liquid hydrocarbon over catalyst at 320-340° yielded a liquid catalyzate by distillation of which a fraction with a b.p. of 140-148° (38 mm) was obtained which quickly crystallized. The crystals were shown to be diphenyl; m.p. 69°, yield around 40%. Fluorene (m.p. 115°) was in the residue after distilling off this fraction. The total yield of fluorene amounted to around 40%.

The benzamino derivative was isolated in the form of two modifications – lusterless crystals with a m.p. of 183-184° and shiny needles which melted at 168-169°. Neither form consisted of a single substance.

Condensation of 3-Methylcyclopentanol with Benzene Under Mild Conditions

The following were taken for the reaction: 3-methylcyclopentanol 2.4 g (0.024 mole), benzene 53 g (0.68 mole), $AlCl_3$ 2.8 g (0.021 mole). Aluminum chloride was added over a period of 1 hour. The mixture stood for 40 hours at room temperature and then was heated for 2 hours, initially on a warm water bath and then at 80°. The products were isolated in the usual manner. 2.15 g (56%) of 1-methyl-3-phenylcyclopentane was obtained:

B.p. 105-106° (16 mm); d_4^{20} 0.9251; n_D^{20} 1.5142; MR_D 52.13; calculated 51.82.

Samples of 1-methyl-3-phenylcyclopentane are described in the literature as having the following constants: b.p. 230-235°; d_4^{17} 0.950; n_D^{17} 1.5276; b.p. 230-232°; d_4^{16} 0.937; n_D^{16} 1.5210; b.p. 93-94° (12 mm); d_4^{17} 0.9173; n_D^{17} 1.5136 [10].

The acetamino derivative was prepared in the usual way. During its crystallization, flakes (chiefly) and lusterless globules precipitated from the diluted alcohol. During further purification of the flakes by crystallization from a mixture of benzene and petroleum ether, fine needle-like crystals with a m.p. of 150-151° were obtained.

6.34 mg sub.: 0.406 ml N_2 (26°, 726 mm). Found %: N 6.79. $C_{14}H_{19}ON$. Calculated %: N 6.49.

Benzamino derivative. Two sorts of crystals precipitated during crystallization from alcohol – transparent fine needles and lusterless globules (chiefly). It was not possible to separate them completely by mechanical means and, therefore, the entire mixture was further crystallized as a whole. After repeated crystallization, the melting point reached 188-189° (fine lusterless needles, grouped in globules).

11.98 mg sub.: 0.628 ml N_2 (26°, 726 mm). Found %: N 5.55. $C_{19}H_{21}ON$. Calculated %: N 5.02.

Condensation of 3-Methylcyclopentanol with Benzene Under Severe Conditions

The following were taken for the reaction: 3-methylcyclopentanol 7 g (0.07 mole), benzene 40 g (0.5 mole), $AlCl_3$ 8.7 g (0.065 mole). Aluminum chloride was added considerably faster than in the preceding case. The evolution of HCl and spontaneous heating of the reaction mixture were, thereupon, observed. Immediately after the addition of all the $AlCl_3$, the reaction mixture was heated on a water bath to the boiling point for 2 hours. 3.4 g (30%) of 1-methyl-4-phenylcyclopentane was obtained:

b.p. 114-116° (24 mm); d_4^{20} 0.9250; n_D^{20} 1.5120; MR_D 51.95; calculated 51.82.

The acetamino derivative was purified analogously to the preceding. Flakes with a m.p. of 151° were obtained. A mixed sample with the acetamino derivative obtained from the product of the preceding condensation did not display melting point depression.

The benzamino derivative after repeated crystallization from alcohol had a m.p. of 187-189°.

SUMMARY

The condensations of 2-methylcyclohexanol and 3-methylcyclopentanol with benzene in the presence of aluminum chloride were studied under various conditions.

It was shown that in the case of 2-methylcyclohexanol, the reaction can proceed in two directions. Under mild conditions (large excess of benzene, slow addition of aluminum chloride, and low temperature) the condensation partially proceeds without isomerization of the alcohol radical; the reaction products are 1-methyl-2-phenylcyclohexane (apparently, a mixture of the cis and trans forms) and 1-methyl-1-phenylcyclohexane. Under more severe conditions, 1-methyl-1-phenylcyclohexane is formed almost exclusively.

The condensation of 3-methylcyclopentanol with benzene under analogous conditions is not accompanied by appreciable isomerization of the alcohol radical.

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* See Consultants Bureau Translation, page 1463.

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*** See Consultants Bureau Translation, page 1257.

PHOTOREACTIONS OF METALLOORANIC COMPOUNDS OF MERCURY IN SOLUTIONS

XIV. PHOTOREACTIONS OF β-MERCURIBISPROPIONIC ACID AND ITS DIMETHYL ESTER

G. A. Razuvaev, Yu. A. Oldekop and V. N. Latyaeva

In a number of preceding works, we have investigated the photoreactions of Ar_2Hg and Alk_2Hg in solutions, which proceed via the formation of free radicals. The radicals which are formed react both with the solvent and with each other, depending on their nature. The photodecomposition of diethylmercury and diphenethylmercury [1] proceeds with the disproportionation of the ethyl radicals into ethane and ethylene, or of phenethyl radicals into styrene and ethylbenzene, keeping pace with the splitting off of hydrogen radicals from the solvent – the basic reaction for methyl and phenyl radicals. In addition to these reactions, the dimerization of radicals should be noted, as it occurs for the benzyl radical [2]. It seemed to us of interest to investigate the influence of functional groups on the reactivity of the radical. We selected β-mercuribispropionic acid and its dimethyl ester as an example. This compound, obtained for the first time by Fischer [3], is completely nontoxic and, therefore, has found application in medicine [4]. However, the chemical properties of this acid have hardly been sufficiently described.

β-Mercuribispropionic acid was prepared by us by Fischer's method, starting from the methyl ester of β-iodopropionic acid and 0.5% sodium amalgam. The dimethyl ester of β-mercuribispropionic acid was isolated for the first time in the pure form.

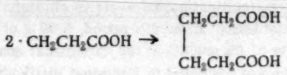
The photoreaction of β-mercuribispropionic acid was investigated in solutions of methanol and the monoethyl ether of ethyleneglycol. The photoreaction proceeded with the evolution of mercury and the formation of propionic and adipic acids. The propionic acid was obtained due to the dehydrogenation by the β-carboxyethyl radical of the solvent alcohol with the formation of formaldehyde or of acetaldehyde. The disproportionation reaction of the radicals which should yield propionic and acrylic acids, was not observed by us. The reaction involving the splitting off of hydrogen prevailed. The course of the reaction can be represented by the following scheme:

$$Hg(CH_2CH_2COOH)_2 \xrightarrow{h\nu} \cdot CH_2CH_2COOH + \cdot HgCH_2CH_2COOH \qquad (1)$$

$$\cdot HgCH_2CH_2COOH \rightarrow Hg + \cdot CH_2CH_2COOH \qquad (2)$$

$$2 \cdot CH_2CH_2COOH + CH_3OH \rightarrow CH_2O + 2CH_3CH_2COOH \qquad (3)$$

(chief reaction ~⅔)



$$2 \cdot CH_2CH_2COOH \rightarrow \begin{array}{l} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{array} \qquad (4)$$

(side reaction ~⅓)

The photoreaction with the dimethyl ester of β-mercuribispropionic acid proceeds analogously. The presence of a gradual splitting off of radicals (reactions 1 and 2) is indicated by the photoreaction of this ester in chloroform, during which β-carbomethoxyethylmercury chloride and the methyl ester of propionic acid were isolated; the radicals formed according to equation (1) react with chloroform with the removal of chlorine (5) and hydrogen (6):

$$\cdot HgCH_2CH_2COOCH_3 + CHCl_3 \rightarrow (\cdot CHCl_2) + ClHgCH_2CH_2COOCH_3 \qquad (5)$$

$$\cdot CH_2CH_2COOCH_3 + CHCl_3 \rightarrow \cdot CCl_3 + CH_3CH_2COOCH_3. \qquad (6)$$

In addition, mercury (in accord with equation 2) and calomel, formed due to the chlorinating action of chloroform on mercury during the irradiation were found.

The ester of adipic acid was not found in the reaction products. Thus, in this case only the splitting off of the hydrogen of the β-carbomethoxyethyl radicals occurs.

This kind of reaction is impossible in benzene solution. And, actually, during the irradiation of the dimethyl ester of β-mercuribispropionic acid in benzene, mercury and the dimethyl ester of adipic acid were isolated. Thus, reactions (1), (2) and (4) occurred. It is of interest to note that by the introduction of a carboxyl group into the ethyl radical, the disproportionation reaction is entirely suppressed, which has great significance in the photoreactions of diethylmercury and diphenethylmercury.

EXPERIMENTAL

The reaction was carried out in thin quartz test tubes with an internal diameter of 18 mm; the illumination was produced by a mercury-quartz lamp (Original Hanau, Hohen Sonne).

Photoreaction of β-mercuribispropionic acid in methanol. 3.0 g of β-mercuribispropionic acid in 20 ml of methanol was illuminated for 100 hours. In the reaction period 1.13 g of metallic mercury, or 97.6% of the theoretical quantity, was isolated. The mercury was filtered off (the filtrate did not decolorize bromine water); the filtrate was subjected to redistillation on a water bath and the distillate gave the silver mirror reaction. In addition, the dimedone formaldehyde derivative was obtained with a m.p. of 187°. Water was added to the residue after distilling off the methyl alcohol, and adipic acid, thereupon, precipitated. After recrystallizing it from ethyl acetate, it had a m.p. of 144°. A mixed sample with adipic acid displayed no melting point depression.

The weight of the adipic acid obtained was 0.2 g, or 23.8% of the theoretical. The aqueous solution obtained after isolating the adipic acid had an acid reaction(decolorization of bromine water was not observed); it was back titrated. 61.2 ml of 0.1 N KOH was consumed in the titration, which corresponded to 0.45 g of propionic acid, or 52.4% of the theoretical quantity.

Analysis of the silver salt:

0.3086 g sub.: 0.1825 g Ag. Found %: Ag 59.14. $C_3H_5O_2Ag$. Calculated %: Ag 59.66.

Photoreaction of β-mercuribispropionic acid in the monoethyl ether of ethylene glycol. 5.0 g of β-mercuribispropionic acid in 25 ml of the monoethyl ether of ethylene glycol was irradiated for 100 hours. 2.85 g of mercury was isolated after this period, which amounted to 98.3% of the theoretical quantity. The filtrate obtained after isolation of the mercury showed an aldehyde reaction (silver mirror). The dimedone acetaldehyde derivative was also isolated with a m.p. of 135°. The filtrate was diluted with water; a precipitate of adipic acid thereupon fell out, which, after recrystallization from ethyl acetate, had a m.p. of 144°. There was no melting point depression of this substance mixed with adipic acid. The weight of the acid obtained was 0.56 g, or 26.4% of the theoretical quantity.

Propionic acid was determined in the aqueous solution. 210.0 ml of 0.1 N KOH was consumed in the titration, which corresponded to 1.55 g of propionic acid, or 72.9% of the theoretical quantity. To identify the propionic acid, its p-bromophenacyl derivative was prepared and had a m.p. of 61°. A mixed sample of this substance with the derivative obtained from known propionic acid exhibited no melting point depression. A test for an unsaturated compound (bromine water) gave a negative result.

Photoreaction of the dimethyl ester of β-mercuribispropionic acid in chloroform. 5.0 g of the dimethyl ester in 25 ml of chloroform was irradiated for 24 hours. After this period, 0.92 g of metallic mercury and 0.2 g of calomel were isolated, which corresponded to 31.8% and 6% of the theoretical quantity, respectively. The mercury and calomel were filtered off. The filtrate was subjected to fractional distillation from a Würtz flask, and the 60-82° range fraction was collected. The residue after distilling off the solvent was subjected to steam distillation. The distillate consisted of the dimethyl ester of β-mercuribispropionic acid and had the characteristic camphor odor due to the presence of a small quantity of hexachloroethane.

The residue from the steam distillation consisted of a yellowish liquid from which β-carbomethoxyethylmercury chloride crystallized out on standing. It was filtered off and had a melting point of 60° (from acetone). There was no melting point depression of this substance with specially prepared β-carbomethoxyethylmercury chloride. 1.0 g of β-carbomethoxyethylmercury chloride or 22.5% of the theoretical was obtained. The filtrate after isolation of the β-carbomethoxyethylmercury chloride consisted of unreacted dimethyl ester of β-mercuribispropionic acid, and together with the distillate from the steam distillation, amounted to 1.9 g, or 38% of the initial quantity. 0.3 g of the methyl ester of propionic acid with a b.p. of 79-81° could be isolated from the fraction which boiled in the 60-82° range in an effective column. The benzylamino derivative of this ester was prepared for identification and melted at 43°, which corresponded with the literature data.

Photoreaction of the dimethyl ester of β-mercuribispropionic acid in benzene. 5.0 g of the dimethyl ester of β-mercuribispropionic acid in 25 ml of benzene was irradiated for 300 hours. The metallic mercury – 2.63 g (quantitative yield) – was filtered off. After distilling off the benzene from the filtrate 2.13 g of the ester of adipic acid was left and was saponified. Adipic acid was isolated in a yield of 90% with a m.p. of 149° after recrystallization from ethyl acetate. There was no melting point depression with known adipic acid.

SUMMARY

1. Quantitative evolution of mercury occurs during the irradiation with ultraviolet light of solutions of β-mercuribispropionic acid in methanol or in the monoethyl ether of ethylene glycol. Due to the splitting off of hydrogen from the solvent, the carboxyethyl radicals form propionic acid and, as a result of the dimerization of these radicals, adipic acid is formed. Aldehydes were detected in both cases.

2. The formation of β-carbomethoxyethylmercury chloride and the methyl ester of propionic acid occurs during the photoreaction of the dimethyl ester of β-mercuribispropionic acid in chloroform. Mercury and calomel were also detected.

3. Only adipic acid and mercury were found upon the photoreaction of the dimethyl ester of β-mercuribispropionic acid in benzene.

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* See Consultants Bureau Translation, page 1489.

REACTION OF ACYL PEROXIDES WITH METALS AND METAL CHLORIDES

(TIN AND ANTIMONY)

G. A. Razuvaev, B. N. Moryganov, E. P. Dlin and Yu. A. Oldekop

The decomposition of perbenzoic acid in solutions is ordinarily represented as involving the evolution of CO_2 and the formation of two radicals C_6H_5 and C_6H_5COO. However, on the basis of more detailed study it can be considered that the evolution of CO_2 is a secondary process; initially dissociation of the O−O bond occurs and then the benzoate radical loses CO_2. There are a number of works in which the reaction of peroxides proceeding without evolution of CO_2 is described. Thus, the reaction of perbenzoic acid in alcohol or in benzene and in their mixtures in the presence of hydroquinone [1], with triphenylbismuth [2], and with metallic mercury in benzene solution [3] all proceed.

In the present work we have investigated the reaction of perbenzoic acid with stannous dichloride, antimony trichloride, and with metallic tin, and also the reaction of acetyl peroxide with antimony. It has previously been indicated that perbenzoic acid reacts with stannous dichloride but the reaction products were not isolated [4].

We investigated the reaction of stannous dichloride with peroxide dissolved in benzene, dichloroethane and acetic anhydride. Perbenzoic acid quantitatively reacted with stannous dichloride without evolution of CO_2 at ordinary temperatures according to the equation

$$(C_6H_5COO)_2 + SnCl_2 \rightarrow (C_6H_5COO)_2SnCl_2.$$

By carrying out the reaction in benzene solution during heating, the perbenzoic acid reacted with stannous dichloride also, while only insignificant CO_2 evolution was observed at the same time. It is of interest to note that during the reaction of perbenzoic acid with metallic tin or with stannous dichloride in benzene during heating, the peroxide does not react at all with benzene. As preliminary experiments showed, antimony trichloride in benzene solution reacts analogously; the addition of the benzoate radicals to Sb^{III} proceeds with conversion into Sb^{V}. At the same time, the reaction of perbenzoic acid with benzene is suppressed.

Perbenzoic acid reacted with metallic tin during the heating in benzene solution. The benzoate radicals added to tin with the formation of the benzoate of tetravalent tin. However, this compound was shown to be very sensitive to the action of moisture and as a result of the reaction only a substance very close in analysis to the product of its hydrolysis could be isolated:

$$2(C_6H_5COO)_2 + Sn \rightarrow (C_6H_5COO)_4Sn \xrightarrow{H_2O} (C_6H_5COO)_2Sn(OH)_2.$$

By heating perbenzoic acid with tin without solvent, the formation of tin benzoate also proceeds, but the greater portion of the peroxide is decomposed into diphenyl and CO_2.

Acetyl peroxide readily reacts with metallic antimony during heating in benzene solution. The very readily hydrolyzed antimony acetate was isolated.

EXPERIMENTAL

Thermal Reaction of Perbenzoic Acid with Stannous Dichloride in Benzene

18.9 g (0.1 mole) of stannous chloride, 24.2 g (0.1 mole) of perbenzoic acid and 200 ml of benzene were simultaneously placed in a three necked flask with a stirrer. The reaction mass was heated to the boiling point of benzene while being stirred for 20 hours. Even a half-hour after the beginning of the experiment, the solution noticeably darkened. 0.09 g of CO_2 (2% of the theoretical) was evolved in the course of the experiment.

Upon completion of the reaction tests for peroxide and Sn^{II} gave negative results. After distilling off the benzene, a dark brown precipitate (43 g) remained; by saponification with hot benzene, 18.6 g of pure stannic dichlorodibenzoate was obtained or 43.1% of the theoretical. The solvent which was distilled off contained stannic chloride, the quantity of which was determined as AgCl. 1.1967 g of AgCl was obtained, which corresponded to 0.54 g of $SnCl_4$.

Stannic dichlorodibenzoate dissolved on heating in chloroform, dichloroethane, and acetone, was poorly soluble in alcohol and benzene, and entirely insoluble in water. The substance did not melt at 330°. Benzoic acid was isolated by the action of hydrochloric acid. A small quantity of precipitate was heated in a test tube with concentrated hydrochloric acid until it dissolved. Benzoic acid with a m.p. of 119° was evolved. A mixed sample with pure benzoic acid had a m.p. of 120°. A precipitate of stannic sulfide settled out from the filtrate during the passage of hydrogen sulfide through it. The substance formed sodium benzoate as a result of the action of sodium hydroxide on it. Benzoic acid was also obtained by the action of steam on the stannic dichlorodibenzoate.

Found %: Cl 15.80; $C_{14}H_{10}O_4SnCl_2$. Calculated %: Cl 16.44. Found %: C 35.20. 34.65; H 2.73, 2.50; Sn 25.58, 26.40. $C_{14}H_{10}O_4SnCl_2$. Calculated %: C 38.91; H 2.31; Sn 27.49.

Reaction of Perbenzoic Acid with Stannous Chloride in Benzene Without Heating

6.3 g (0.033 mole) of anhydrous stannous chloride, 8.0 g (0.033 mole) of recrystallized perbenzoic acid and 50 ml of benzene were placed in a flask with a ground stopper. The mixture was shaken on a machine. Even a half hour after beginning, the shaking the solution blackened. After shaking for 12 hours, all the peroxide had reacted. The benzene was distilled off from the reaction mixture. Tetravalent tin was determined in it. 0.6241 g of AgCl which corresponded to 0.28 g of $SnCl_4$ was obtained. The residue after distilling off the benzene weighed 14.0 g, from which 4.82 g of pure $(C_6H_5COO)_2SnCl_2$ or 33.7% of the theoretical was isolated by washing off with hot benzene.

Reaction of Perbenzoic Acid With Stannous Chloride in Dichloroethane and In Acetic Anhydride Without Heating

The reaction was carried out in dichloroethane and also in acetic anhydride under the same conditions. 3.16 g (0.013 mole) of recrystallized perbenzoic acid, 2.46 g (0.013 mole) of stannous chloride and 50 ml of solvent were taken. The contents of the flask were shaken for 2 hours on a machine and then, after distilling off the solvent, 5.1 and 4.7 g of raw product respectively, was isolated. 1.69 pure $(C_6H_5COO)_2SnCl_2$ was isolated from the 5.1 g of crude product. The solvent distilled off (dichloroethane and acetic anhydride) did not contain $SnCl_4$.

Thermal Reaction of Perbenzoic Acid With Antimony Trichloride in Benzene

By heating equimolecular quantities of antimony trichloride and perbenzoic acid in benzene the antimony was entirely converted from Sb^{III} into Sb^{V}. Noticeable quantities of CO_2 were not detected. During the treatment of the product obtained with hydrochloric acid the theoretical quantity of benzoic acid was evolved.

Thermal Reaction of Perbenzoic Acid With Metallic Tin in Benzene

250 ml of benzene and 10 g of powdered metallic tin were placed in a three-necked flask supplied with a mechanical stirrer with a mercury seal. The benzene was brought to boiling and during continuous stirring in the flask over a period of 4 hours, 20 g of perbenzoic acid (activity 93%) was introduced in small portions. The heating and stirring were continued for 13 more hours after this. Even a half hour after the beginning of the addition of the peroxide, darkening of the liquid was observed, which then became dark brown. Upon completion of the reaction a test for peroxide gave a negative result. Only traces of CO_2 were evolved during the reaction. The reaction mass consisted of a grey residue that was insoluble in benzene. The benzene layer was poured off from the residue, filtered and redistilled on a water bath. Alkali was added to the residue and steam passed through it. Upon completion of the steam distillation, the alkaline solution was filtered off, condensed to small volume after which it was acidified with hydrochloric acid. 1 g of benzoic acid with a m.p. of 121° (from water) was isolated. A mixed sample with pure benzoic acid gave a m.p. 121°. After the benzene had been separated from the water, it was subjected to redistillation, which demonstrated the absence of any other products in it. The grey precipitate obtained as a result of the reaction was filtered off and washed with benzene. It was shown to be poorly soluble in alcohol, acetone, ethylcellulose, ethyl ether, carbon tetrachloride, benzene, etc.. No appreciable changes were observed as a result of the action of caustic alkali or hydrochloric acid. The substance was shown to be rather soluble in dichloroethane and, therefore, it was subjected to extraction with this solvent in a Soxhlet apparatus. 14.3 g of a white crystalline substance was thus obtained which in analysis and properties fitted the formula $(C_6H_5COO)_2Sn(OH)_2$.

Found %: C 44.90, 45.08; H 2.90, 3.32; Sn 29.10, 29.80. $C_{14}H_{12}O_6Sn$. Calculated %: C 42.56; H 3.04; Sn 30.07.

This substance did not melt at temperatures up to 330°; however even at much lower temperatures cleavage of benzoic acid occurred, after which an infusible amorphous precipitate remained. The evolution of benzoic acid was observed as a result of the action of steam on this substance. Thus, 121 g of benzoic acid or 82.3% calculating on the basis of $(C_6H_5COO)_2Sn(OH)_2$ was obtained from a sample of 2.36 g. An analogous result was obtained by preliminary alkalinization of the sample. Benzoic acid was cleaved off by heating the precipitate with concentrated hydrochloric acid to 130-140° in a sealed tube.

Reaction of Perbenzoic Acid With Metallic Tin Without Heating

5 g of tin, 5 g of perbenzoic acid and 40 ml of benzene were shaken on a machine for 150 hours. The reactants were isolated unchanged.

Thermal Reaction of Perbenzoic Acid With Metallic Tin Without Solvent

0.1 g of perbenzoic acid with excess metallic tin was heated on a sand bath. The decomposition of the peroxide proceeded with detonation and evolution of CO_2. Crystals of diphenyl with a m.p. of 64-65° separated on the walls of the test tube on cooling. This substance was fused with pure diphenyl at 65°. The solid reaction products were extracted with dichloroethane. On evaporating off the dichloroethane a substance remained which was insoluble in the majority of organic solvents and was analogous to the substance from the experiment which was carried out in benzene solution with heating.

Thermal Reaction of Acetyl Peroxide With Metallic Antimony in Benzene*

10 g of metallic antimony and 8.7 g of acetyl peroxide in 100 ml of benzene were placed in a three-necked flask supplied with a mechanical stirrer with a mercury seal. The reaction mass was heated and stirred for 8 hours. 0.08 g of CO_2 was evolved in the course of the reaction. A test for the presence of peroxide gave a negative result. Colorless crystals separated on cooling the reaction mass, which were separated from the unreacted antimony (4.8 g). The crystals, which consisted of antimony triacetate, were transferred to a vacuum desiccator and dried. Sb^V ions were not found. This substance very rapidly underwent hydrolysis in air. The hydrolysis products consisted of antimony trioxide and acetic acid. The same sort of decomposition occurred during the action of aqueous alcohol. The antimony triacetate from the vacuum desiccator was treated with ethyl alcohol and back titrated with 0.1 N NaOH. 7.2 g of acetic acid was contained in it which was equivalent to 12.1 g of antimony triacetate. Thus, according to the triacetate formed, 4.9 g of antimony entered into the reaction. The quantity of antimony which reacted as found by the difference in the charge and in the residue was 5.1 g.

SUMMARY

1. Perbenzoic acid yields $(C_6H_5COO)_2SnCl_2$ with stannous chloride in benzene, dichloroethane and acetic anhydride solution. $SbCl_3$ reacts analogously.

2. Perbenzoic acid in benzene solution, reacts with metallic tin during heating without CO_2 evolution, and with the formation of stannic tetrabenzoate. Its hydrolysis product $(C_6H_5COO)_2Sn(OH)_2$ was isolated.

3. Antimony triacetate was formed by heating antimony with a benzene solution of acetyl peroxide.

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* E. A. Sheer completed the reaction of peroxide with Sb and $SbCl_3$.

** See Consultants Bureau Translation, page 613.

[illegible]

[illegible]

Thermal Reaction of Perrhenic Acid With Metallic Tin [illegible]

[illegible]

[illegible]

SUMMARY

1. Perrhenic acid [illegible]

2. Perrhenic acid in benzene solution reacts with metallic tin during heating [illegible]

3. Antimony [illegible]

LITERATURE CITED

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

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* [illegible]

** See Consultants Bureau Translation, [illegible]

REACTION OF METHYL-α-NAPHTHYLMERCURY AND METHYLPHENYLMERCURY WITH ORGANIC ACIDS[*]

A. A. Bolshakova

Cahours [1] and Otto [2] studied for the first time the reaction of alkyl and aryl compounds of mercury with acetic acid,and showed that the corresponding acetates and hydrocarbons were thereby formed. Melnikov and Rokitskaya [3] investigated the reaction of compounds of the R_2Hg type with mercury salts of dibasic and tribasic acids. Koton [4, 5] studied in great detail the reaction of diphenylmercury and di-α-naphthylmercury with monobasic organic acids,and gave as the general reaction equation

$$(C_6H_5)_2Hg + HOCOR \rightarrow C_6H_6 + C_6H_5\,HgOCOR.$$

They further investigated [6] the reaction of dimethyl mercury with organic acids,and showed that, during heating for 3 hours at 130°,derivatives of the acids containing the $CH_3Hg\cdot$ radical were formed,and methane was evolved. Chernov [7, 8] studied the reaction of organic acids with di-o- and di-p-tolylmercury. He succeeded in all cases in observing the formation of derivatives of the RHgOCOR type where RHg· is the o- or p-tolylmercury radical,and the evolution of toluene.

It was of interest to study the reaction with organic acids of asymmetric organomercury compounds in the example of methyl-α-naphthylmercury and methylphenylmercury,and to establish which of the radicals which enter into the composition of these compounds is the most reactive.

A crystalline substance with a definite melting point is formed during the reactions of methyl-α-naphthylmercury and methylphenylmercury with organic acids. The reaction proceeds during heating to 75° for 6 hours. On the basis of the experimental data, the mechanism of the reaction can be represented by the following scheme

$$CH_3HgR \rightarrow CH_3Hg\cdot + R\cdot$$

$$R\cdot + HOCOR' \rightarrow RH + \cdot OCOR'$$

$$CH_3Hg\cdot + \cdot OCOR' \rightarrow CH_3HgOCOR',$$

where R' is the α-naphthyl or phenyl radical, while RH is,respectively,naphthalene or benzene. According to the analytical results, the derivatives obtained for dibasic acids contained two $CH_3Hg\cdot$ radicals and substituted hydrogens on both carboxyl groups. The experimental data permit one to conclude that the less reactive methyl radical remains bound to a mercury atom,and in such a form is transferred into the composition of the acid derivative. The more reactive α-naphthyl and phenyl radicals are torn off from the mercury and form naphthalene or benzene with a hydrogen atom. Consequently, the behavior of the methyl, α-naphthyl and phenyl radicals during the reactions of their asymmetric organomercury compounds is in complete agreement with the position of each of them in the Nesmeyanov-Kharasch series. It should also be noted that asymmetric compounds studied by us react with organic acids at a greater rate (even at 75°) than symmetric mercury compounds with which the reaction proceeds at 100 and 130°.

EXPERIMENTAL

I. Synthesis of Methyl-α-naphthylmercury and Methylphenylmercury

Methyl-α-naphthylmercury was synthesized by the method of Freidlina, Nesmeyanov and Kocheshkov [9]: it consisted of fine, colorless crystals with a m.p. of 82° (according to Nesmeyanov 84°).

0.0492 g sub.: 2.86 ml 0.1 N NH_4CNS. Found %: Hg 58.13. $C_{11}H_{10}Hg$. Calculated %: Hg 58.55.

Methylphenylmercury was prepared by the action of C_6H_5MgBr on CH_3HgI [10]. Methylphenylmercury is a heavy, transparent liquid. In view of the thermal instability of methylphenylmercury, its identification was carried out by treatment with an alcoholic solution of hydrogen chloride. Methylmercury chloride with a m.p. of 170-171° (according to the literature data 171°) was thereby quantitatively formed. A mixed sample with the known substance had a m.p. of 170°.

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[*] Abstract from the candidate's dissertation of A. A. Bolshakova.

All the experiments involving the study of the reaction of mercury compounds with organic acids were carried out in sealed glass ampoules during heating to 75° for 6 hours.

II. Reaction of Methyl-α-naphthylmercury with Organic Acids

1. Stearic acid. 0.15 g stearic acid and 0.2 g of methyl-α-naphthylmercury were taken. With benzene 0.06 g of a white substance with a m.p. of 80-81° was isolated.

0.0510 g sub.: 2.03 ml 0.1 N NH_4CNS. Found %: Hg 39.80. $C_{17}H_{35}COOHgCH_3$. Calculated %: Hg 40.23.

2. Adipic acid. The mixture was heated for 3 hours at 100°. 0.1 g of adipic acid was taken for 0.2 g of methyl-α-naphthylmercury. With hot water 0.06 g of a white crystalline substance with a m.p. of 171-173° was isolated.

0.0500 g sub.: 3.48 ml 0.1 N NH_4CNS. Found %: Hg 69.60. $(CH_2)_4(COOHgCH_3)_2$. Calculated %: Hg 69.73.

3. Salicylic acid. 0.1 g of salicyclic acid was taken for 0.2 g of methyl-α-naphthylmercury. With hot aqueous alcohol 0.05 g of a white crystalline substance with a m.p. of 112-114° was obtained.

0.0350 g sub.: 1.98 ml 0.1 N NH_4CNS. Found %: Hg 56.57. $C_6H_4(OH)COOHgCH_3$. Calculated %: Hg 56.89.

4. Phthalic acid. 0.1 g of phthalic acid and 1 drop of water were taken for 0.2 g of methyl-α-naphthylmercury. With hot alcohol 0.07 g of a crystalline substance with a m.p. of 223-224°, with decomposition, was isolated.

0.0512 g sub.: 3.45 ml 0.1 N NH_4CNS. Found %: Hg 67.18. $C_6H_4(COOHgCH_3)_2$. Calculated %: Hg 67.44.

Naphthalene was detected in all the experiments, and its presence demonstrated in the usual way.

III. Reaction of Methylphenylmercury with Organic Acids

1. Butyric acid. 0.5 ml of butyric acid was taken for 0.15 g methylphenylmercury. The reaction mass was a liquid. On adding water white flaky crystals separated from the reaction mass on standing. After recrystallization from alcohol 0.04 g of white flaky crystals with a m.p. of 44-45° was obtained.

0.0330 g sub.: 1.98 ml 0.1 N NH_4CNS. Found %: Hg 66.00. $CH_3(CH_2)_2COOHgCH_3$. Calculated %: Hg 66.29.

2. α-Hydroxybutyric acid. 0.5 ml of α-hydroxybutyric acid was taken for 0.15 g of methylphenylmercury. 0.09 g of a white crystalline substance with a m.p. of 96-97° was isolated with water from the reaction mass during prolonged standing.

0.0500 g sub.: 3.14 ml 0.1 N NH_4CNS. Found %: Hg 62.80. $CH_3CH_2CH(OH)COOHgCH_3$. Calculated %: Hg 62.96.

3. Nonylic acid. 0.5 ml of nonylic acid was taken for 0.15 g of methylphenylmercury. 0.1 g of yellowish crystals with a m.p. of 45-46° was isolated from the reaction mixture.

0.0500 g sub.: 2.49 ml 0.1 N NH_4CNS. Found %: Hg 49.80. $CH_3(CH_2)_7COOHgCH_3$. Calculated %: Hg 50.58.

4. Palmitic acid. 0.15 g of palmitic acid was taken for 0.15 g of methylphenylmercury. 0.11 g of a white substance with a m.p. of 72-73° was isolated with hot alcohol.

0.0500 g sub.: 2.11 ml 0.1 N NH_4CNS. Found %: Hg 42.20. $C_{15}H_{31}COOHgCH_3$. Calculated %: Hg 42.62.

5. Stearic acid. 0.15 g of stearic acid was taken for 0.15 g of methylphenylmercury. 0.1 g of a white substance with a m.p. of 80-81° was isolated with hot alcohol.

0.0500 g sub.: 2.00 ml 0.1 N NH_4CNS. Found %: Hg 40.00. $C_{17}H_{35}COOHgCH_3$. Calculated %: Hg 40.23.

6. Adipic acid. 0.2 g of adipic acid was taken for 0.2 g of methylphenylmercury. 0.1 g of a white crystalline substance with a m.p. of 171-173° was isolated with hot water.

0.0500 g sub.: 3.47 ml 0.1 N NH_4CNS. Found %: Hg 69.40. $(CH_2)_4(COOHgCH_3)_2$. Calculated %: Hg 69.74.

7. Citric acid. 0.15 g of citric acid was taken for 0.15 g of methylphenylmercury. Heating was continued for 1 hour at 100°. 0.09 g of a white crystalline substance which decomposed at 139° was isolated with alcohol.

0.0520 g sub.: 3.33 ml 0.1 N NH_4CNS. Found %: Hg 64.04. $C(OH)(COOH)(CH_2COOHgCH_3)_2$. Calculated %: Hg 64.58.

8. Benzoic acid. 0.1 g of benzoic acid was taken for 0.15 g of methylphenylmercury. 0.09 g of a white crystalline substance with a m.p. of 105-106° was isolated with ether.

0.0500 g sub.: 2.97 ml 0.1 N NH_4CNS. Found %: Hg 59.40. $C_6H_5COOHgCH_3$. Calculated %: Hg 59.59.

9. Salicylic acid. 0.15 g of salicylic acid was taken for 0.2 g of methylphenylmercury. 0.11 g of white crystals with a m.p. of 112-114° was isolated.

0.0500 g sub.: 2.82 ml 0.1 N NH_4CNS. Found %: Hg 56.40. $C_6H_4(OH)COOHgCH_3$. Calculated %: Hg 56.89.

10. Phthalic acid. 0.1 g of phthalic acid was taken for 0.15 g of methylphenylmercury. 0.19 g of a white crystalline substance which melted at 223-224°, with decomposition, was isolated with hot alcohol.

0.0600 g sub.: 4.03 ml 0.1 N NH_4CNS. Found %: Hg 67.17. $C_6H_4(COOHgCH_3)_2$. Calculated %: Hg 67.44.

The reaction products of methylphenylmercury with stearic, adipic, salicyclic and phthalic acids were the same as those obtained during the reaction of methyl-α-naphthylmercury with the acids named.

I convey my heartfelt gratitude to M. M. Koton for submitting the theme for the dissertation and for guidance during the completion of the work.

SUMMARY

1. Methyl-α-naphthylmercury and methylphenylmercury form crystalline derivatives of the general formula $CH_3HgOOCR$ during reaction with monovalent acids.

2. Methyl-α-naphthylmercury and methylphenylmercury form crystalline derivatives of the general formula $CH_3HgOOCRCOOHgCH_3$ with dibasic acids.

3. During the reaction of asymmetric compounds of mercury with organic acids, the more reactive radical (naphthyl, phenyl), is first split off to form a hydrocarbon (naphthalene, benzene) with the hydrogen of the acid and the free radicals which are formed then yield the corresponding acyl derivatives.

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* See Consultants Bureau Translation, page 1181.

** See Consultants Bureau Translation, page 345.

*** See Consultants Bureau Translation, page 113.

DESTRUCTIVE HYDROGENATION OF TETRAETHYLSILANE

M. G. Voronkov, B. N. Dolgov and G. B. Karpenko

It was shown a quarter of a century ago by one of the authors [1] that tetraethylsilane when heated to 350-360° under hydrogen pressure, cleaves off ethane and is converted into hexaethyldisilane

$$2Si(C_2H_5)_4 + H_2 \rightarrow (C_2H_5)_3SiSi(C_2H_5)_3 + 2C_2H_6.$$

The formation of silane and, apparently, of higher ethylated silanes is observed along with this.

The hydrogenation of tetraethylsilane in the vapor phase at ordinary pressure was investigated in the present work. It was established in the course of this work that tetraethylsilane is not altered at temperatures up to 500° in an atmosphere of hydrogen in the absence of catalyst. At higher temperatures pyrolysis of the tetraethylsilane proceeds [2] with formation of elementary silicon and gaseous products,and the reaction chiefly proceeds according to the equation $Si(C_2H_5)_4 \rightarrow Si + 4C_2H_4 + 2H_2$. Ethylene pyrolysis products −methane and carbon− are formed simulaneously.

We found during the study of the reaction of tetraethylsilane with hydrogen over various catalysts that over active aluminum silicate catalyst at a temperature close to the initial pyrolysis temperature of tetraethylsilane (550°), its destructure hydrogenation into triethylsilane proceeds:

$$Si(C_2H_5)_4 + H_2 \rightarrow (C_2H_5)_3SiH + C_2H_6.$$

Along with the destructive hydrogenation of tetraethylsilane into triethylsilane, a more profound hydrogenolysis also proceeds with formation of elementary silicon, deposited on the catalyst, and ethane: $Si(C_2H_5)_4 + 2H_2 \rightarrow$ $\rightarrow Si + 4C_2H_6$.

This reaction becomes predominant when the temperature is increased above 600°. At the optimal temperature (550°) the destructive hydrogenation of tetraethylsilane over aluminum silicate catalyst leads to the formation of up to 55% of triethylsilane, calculating on the basis of the condensate obtained. The latter consists of a mixture of $Si(C_2H_5)_4$ and $HSi(C_2H_5)_3$. No other volatile reaction products which condensed at −80° were isolated during the hydrogenolysis of tetraethylsilane over aluminumsilicate catalyst. Thus, neither hexaethyldisilane (the product of the hydrogenation of $Si(C_2H_5)_4$ under pressure, nor the ethylsilanes $(C_2H_5)_2SiH_2$ and $(C_2H_5)SiH_3$ were formed during the destructive hydrogenation of tetraethylsilane. Ethylene −the product of the pyrolysis of tetraethylsilane in the absence of catalyst− was also absent.

The dependence of the yield of triethylsilane on the temperature of the hydrogenation of tetraethylsilane over industrial and synthetic aluminum silicate catalyst is presented in Table 1. These data show that the optimal yield of triethylsilane for both catalysts occurs at 550°; the industrial sample of aluminum silicate catalyst appears to be more active.

TABLE 1

Yields of Triethylsilane During the Destructive Hydrogenation of Tetraethylsilane Over Aluminum Silicate Catalyst

Temp. (in °)	Yield of triethylsilane (in %), calculating on the basis of the initial $Si(C_2H_5)_4$*	
	Industrial catalyst	Synthetic catalyst
350	0	0
400	6	0
450	11	0
500	25	6
530	–	25
550	54	32
580	–	28
600	14	15

---

* Average of analytical determinations by three methods.

The reaction mechanism of the destructive hydrogenation can be represented by the following scheme:

$$(C_2H_5)_4Si \rightarrow (C_2H_5)_3Si\cdot + \cdot C_2H_5 \xrightarrow[\text{aluminum silicate}]{+\,2H} (C_2H_5)_3SiH + C_2H_6.$$

It follows from this scheme that the $(C_2H_5)_3Si-$ and $-C_2H_5$ radicals formed as a result of the pyrolysis are hydrogenated at the surface of the catalyst. In the absence of catalyst, these radicals are decomposed into silicon, ethylene and hydrogen [2], while under hydrogen pressure, they are converted into hexaethyldisilane and ethane. At a high tetraethylsilane hydrogenolysis temperature the triethylsilyl radical is decomposed:

$$(C_2H_5)_3Si\cdot \longrightarrow Si + 3C_2H_5\cdot \xrightarrow{+3H} 3C_2H_6.$$

The ethyl radicals thereby formed are hydrogenated on the catalyst to ethane while the silicon is not changed (as is well known, silicon hardly reacts with hydrogen [3]; silane is completely decomposed into its elements at a temperature above 380° [4]).

EXPERIMENTAL

Tetraethylsilane was obtained in a yield of 83% by the reaction of C_2H_5MgCl with silicon chloride and was carefully purified by Eger's method [5]. After redistillation in a column over sodium it had the following constants: b.p. 152° (760 mm); d_4^{20} 0.7657; n_D^{20} 1.4268.

Triethylsilane was obtained in a yield of 75% by the reaction of C_2H_5MgCl with trichlorosilane [6]. After treatment with sodium in the cold, it was distilled in a column. Its constants were: b.p. 108.0° (756 mm); d_4^{20} 0.7311; n_D^{20} 1.4121.

Catalyst. Industrial aluminum silicate catalyst was used as well as catalyst prepared by the method described in the literature. The latter catalyst turned out to be less effective. The application of nickel, iron and copper to the aluminum silicate catalyst led to lowering the yields of triethylsilane during the destructive hydrogenation of tetraethylsilane.

Experimental methods. The destructive hydrogenation of tetraethylsilane was carried out by a circulating method in the usual catalytic apparatus. Granulated catalyst (volume 75 ml) was placed in a pyrex tube with an internal diameter of 20 mm. The length of the catalyst layer was 28 cm. The catalyst was preliminarily heated in a rapid stream of hydrogen at 450° until the evolution of water had entirely ceased. The tetraethylsilane was passed over the catalyst at a rate of 10 ml/hour, (volumetric rate 16) in a stream of pure dry hydrogen (6 liters/hour). The liquid reaction products were collected in a receiving flask cooled to 0° and supplied with a reflux condenser. The gases formed during the reaction did not contain components which condensed in two successively placed traps which were cooled to −80°. They also did not contain unsaturated compounds or silane (the absence of a reaction with bromine solution and $KMnO_4$) and consisted of ethane and hydrogen. Regeneration of the catalyst was carried out after every 6-8 experiments by passing a stream of dry air through the catalyst, which was heated to 450° until it became white. The activity of the catalyst nevertheless, was somewhat lowered (apparently due to shielding of the active centers with silicon dioxide which was formed by the oxidation of the silicon which was deposited on the catalyst). The experimental data are set forth in Table 1.

Method of analysis. In preliminary experiments the catalyzate was distilled in an analytical column. In all cases it consisted of a two component mixture of triethylsilane and unchanged tetraethylsilane. The triethylsilane isolated during the fractional distillation of the catalyzate had a b.p. of 107.3-108.3°; d_4^{20} 0.7299; n_D^{20} 1.4119.

Found M: 116.4, 117.5. $C_6H_{16}Si$. Calculated M: 116.28. Found %: H (Si) 0.85, 0.86. $(C_2H_5)_3SiH$. Calculated %: H(Si) 0.87.

The absence in the catalyzate of any other compounds besides $Si(C_2H_5)_4$ and $HSi(C_2H_5)_3$ (including resinification products) made it possible to analyze the catalyzate more fully for triethylsilane content. Three methods were used for this.

1) Content in the catalyzate of hydrogen bound to silicon. The determination of the hydrogen bound to silicon in the triethylsilane was carried out by splitting the Si−H bond with alcoholic alkali [7] or with sulfuric acid containing $HgSO_4$. The hydrogen evolved by this treatment of a catalyzate sample was collected and measured in a gas burette over mercury.

2) Elimination of triethylsilane from the catalyzate by sulfuric acid. We found that triethylsilane is readily and completely dissolved in concentrated sulfuric acid with the evolution of hydrogen, and is thereby converted into the H_2SO_4 soluble bis-(triethylsilane)-sulfate and hexaethyldisiloxane. This reaction is catalyzed by mercury salts. In contrast to this, tetraethylsilane is practically insoluble in concentrated H_2SO_4 (0.8 ± 0.2 ml of $(C_2H_5)_4Si$ dissolve in 100 ml of sulfuric acid at 20°). The determination of the content of triethylsilane in the catalyzate treated with sulfuric acid was carried out in a sulfator-burett by the method customarily used in hydrocarbon analysis. The method was verified by artificial mixtures of tetraethylsilane and triethylsilane. In each determination, 5 ml of concentrated H_2SO_4 containing 0.5% $HgSO_4$ was taken and an experimentally found correction factor was introduced for the solubility of tetraethylsilane.

3) Refractive index of the catalyzate. We determined the refractive indices (n_D^{20}) of binary mixtures of triethylsilane and tetraethylsilane. These data, presented in Table 2, show that within the limits of the error of measurement, the dependence between triethylsilane content in the mixture (in percentages by weight) and its

TABLE 2

Refractive Indices of Binary Mixtures of Tetraethylsilane – Triethylsilane

Content of $(C_2H_5)_3SiH$ (in % by weight)	n_D^{20} ± 0.0002
0.0	1.4268
25.7	1.4229
28.4	1.4227
34.0	1.4216
43.0	1.4206
49.9	1.4195
56.4	1.4186
67.5	1.4170
71.1	1.4162
80.2	1.4151
91.9	1.4132
100.0	1.4121

refractive index is determined by the linear equation: $\% (C_2H_5)_3SiH = 6803 (n_D^{20} - 1.4268)$. This equation was employed to determine the triethylsilane content in the catalyzate by its refractive index.

A number of experiments which we carried out under various conditions using various solvents for the volumetric determination of triethylsilane iodometrically, mercurometrically and argentometrically, did not head to satisfactory enough results.

SUMMARY

It was shown that at a temperature close to 550°, tetraethylsilane is cleaved by hydrogen over aluminum silicate catalyst with formation of triethylsilane and ethane.

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[2] C. E. Waring, Trans. Farad. Soc., 36, 1142 (1940); cf. D. F. Helm, E. Mack, J. Am. Chem. Soc., 59, 60 (1937); T. V. Sathyamurthy, S. Swaminathan, L. M. Yeddanapalli, J. Indian. Chem. Soc., 27, 509 (1950).

[3] A. Dufoir, Comptes rend., 138, 1040 (1904).

[4] H. Wartenberg, Z. Electrochem., 18, 658 (1912); Z. allg. anorg. Chem., 79, 71 (1913).

[5] F. M. Jaeger, D. W. Dijkstra, Z. allg. anorg. Chem., 143, 233 (1925).

[6] F. C. Whitmore, E. W. Pietrusza, L. M. Sommer, J. Am. Chem. Soc., 69, 2108 (1947).

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SYNTHESIS OF CERTAIN PHENAMINE DERIVATIVES

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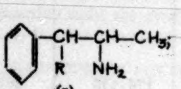
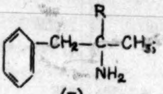
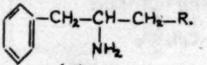
Phenamine derivatives as nervous system stimulants have up to now attracted the attention of pharmacologists, who have tried to establish a relation between the structure and the physiological activity of the given series of compounds.

To resolve this problem, the synthesis of phenamine derivatives with an elongated side carbon chain was accomplished


(I)

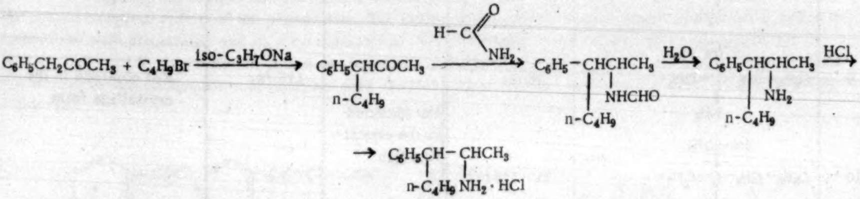

(II)


(III)

The first member of each series was distinguished from the next following member only by the homologous difference which permitted the influence of separate functional groups of the substance on its physiological activity to be established.

In Table 1 are set forth data on the phenamine derivatives synthesized by us, including two compounds obtained for the first time and characterized by us – a compound with the butyl radical on the first carbon atom of the side chain and one with an isobutyl radical on the second carbon atom (Table 1, Nos. 4 and 10).

The phenamine derivative with the butyl radical on the first carbon atom was prepared from methylbenzyl ketone by the Leuckart reaction extended by Suter and Weston [1] to alkylphenylacetones.



The hydrochloride of 2-amino-3-phenylheptane was isolated in two diastereoisomeric forms with m.p. of 148-149 and of 228°, the possibility of the formation of which was due to the presence of two asymmetric carbon atoms.

Along with the low melting form of the hydrochloride (obtained in experiment No. 1) (m.p. 136-139°) described in the literature, a high melting form of the hydrochloride (m.p. 212-212.5°) was isolated. The methyl derivative of the given series – 2-amino-3-phenylbutane was also obtained in two diastereoisomeric forms. With the exception of the phenyl derivative, all the phenamine derivatives with elongated side chains at the first carbon atom were synthesized from the corresponding ketones by the scheme set forth above.

The phenyl derivative was prepared from methylbenzyl ketone by reduction of the ketoxime with metallic sodium in absolute ethyl alcohol

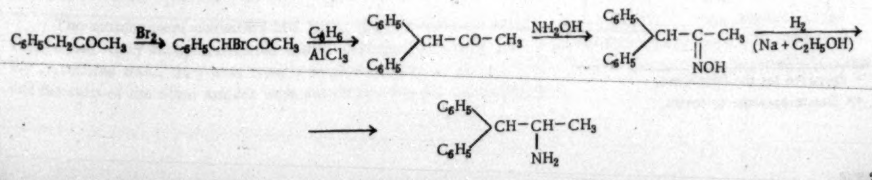
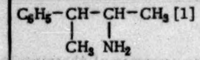
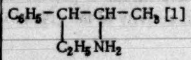
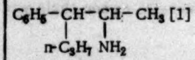
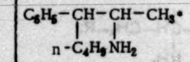
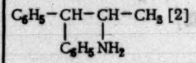
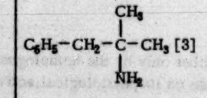
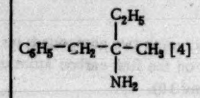
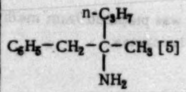
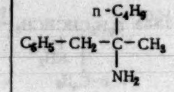
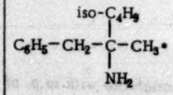
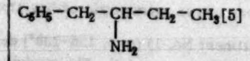
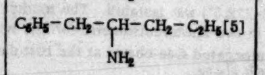
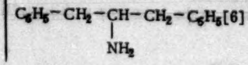


TABLE 1

Expt. No.	Formula of the amine	Boiling point (in °) at pressure (in mm)	Melting point of the hydrochloride (in °)	Literature data	
				Boiling point (in °) at pressure (in mm)	Melting point of the hydrochloride (in °)
1	 $C_6H_5-\underset{CH_3}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$ [1]	100-105 (13)	1) 212-212.5 2) 137-138**	118-119 (19)	136-139
2	 $C_6H_5-\underset{C_2H_5}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$ [1]	107-110 (18)	172-173	118 (19)	1) 171-172 2) 258-261**
3	 $C_6H_5-\underset{n\text{-}C_3H_7}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$ [1]	102-103 (7)	249-250	116 (15)	1) 250-253 2) 120-123**
4	 $C_6H_5-\underset{n\text{-}C_4H_9}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$*	120 (8)	1) 228 2) 148-149**	–	–
5	 $C_6H_5-\underset{C_6H_5}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-CH_3$ [2]	174-180 (20)	278	176-179 (21-23)	280-282
6	 $C_6H_5-CH_2-\overset{CH_3}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$ [3]	65 (3)	198	85-90 (10)	198-198.5
7	 $C_6H_5-CH_2-\overset{C_2H_5}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$ [4]	114 (19)	200		200-201
8	 $C_6H_5-CH_2-\overset{n\text{-}C_3H_7}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$ [5]	118 (10)	161	118 (10)	161
9	 $C_6H_5-CH_2-\overset{n\text{-}C_4H_9}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$	115 (6)	Not obtained in the crystalline form	115 (6)	Not obtained in the crystalline form
10	 $C_6H_5-CH_2-\overset{iso\text{-}C_4H_9}{\overset{\vert}{\underset{NH_2}{\underset{\vert}{C}}}}-CH_3$*	113-114 (14)		–	–
11	 $C_6H_5-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-CH_2-CH_3$[5]	104-113 (6)	141		146
12	 $C_6H_5-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-CH_2-C_2H_5$[5]	102-104 (9)	125-126		131
13	 $C_6H_5-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-CH_2-C_6H_5$[6]	189-193 (13) m.p. 48-49	200	117 (12), m.p. 50	200-202

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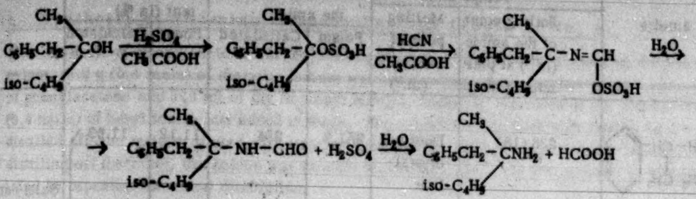
* Prepared for the first time.

** Diastereoisomeric forms.

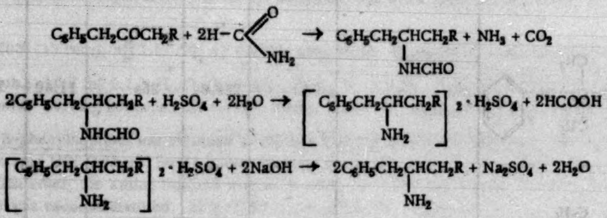
The phenamine derivative with the isobutyl radical at the second carbon atom was prepared by Ritter and Kalisch's reaction [3]:



Other phenamine derivatives with substitutents at the second carbon atom were also synthesized by this reaction.

The synthesis of phenamine derivatives with an elongated side chain at the third carbon atom was accomplished by us by Leuckart's reaction under the conditions described by Magidson and Garkusha [7] The entire synthetic process can be depicted by the following scheme

$$(C_6H_5CH_2COO)_2Ca + (RCH_2COO)_2Ca \rightarrow 2CaCO_3 + 2C_6H_5CH_2COCH_2R$$



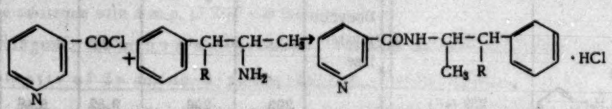
$$C_6H_5CH_2COCH_2R + 2H-C\begin{matrix}\diagup O\\ \diagdown NH_2\end{matrix} \rightarrow C_6H_5CH_2\underset{NHCHO}{\underset{|}{C}}HCH_2R + NH_3 + CO_2$$

$$2C_6H_5CH_2\underset{NHCHO}{\underset{|}{C}}HCH_2R + H_2SO_4 + 2H_2O \rightarrow \left[C_6H_5CH_2\underset{NH_2}{\underset{|}{C}}HCH_2R\right]_2 \cdot H_2SO_4 + 2HCOOH$$

$$\left[C_6H_5CH_2\underset{NH_2}{\underset{|}{C}}HCH_2R\right]_2 \cdot H_2SO_4 + 2NaOH \rightarrow 2C_6H_5CH_2\underset{NH_2}{\underset{|}{C}}HCH_2R + Na_2SO_4 + 2H_2O$$

The pharmacological investigation of the phenamine derivatives showed that the position of the radical on any particular carbon atom of the side chain did not exert significant influence on the change of the properties of the preparation.

The weight of the radical and the substitution of a phenyl radical for an alkyl radical substantially affected the pharmacological activity of the preparation. The phenyl derivative had a more pronounced stimulative action in comparison with phenamine and its alkyl derivatives. With increasing weight of the radical (by substitution in positions 1,2, and 3) the stimulant action on the sympathetic nervous system disappears. Several of the derivatives synthesized by the condensation of nicotinic acid chloride with phenamine were converted into the corresponding amides [8]

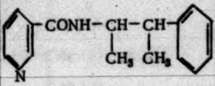
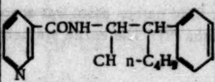
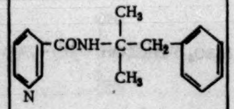
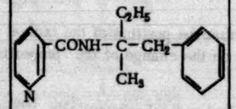
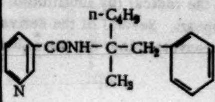
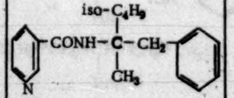
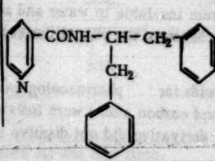


In Table 2, the nicotinic acid amides obtained by us are set forth.

The amides consisted of solid colorless crystalline substances or thick yellowish oils which solidified in the cold into a vitreous mass and crystallized on prolonged standing. The amides were insoluble in water and readily soluble in benzene, dioxane, chloroform, ether, alcohol, and peach oil. The solubility of the phenyl derivative was less.

The amides were converted into the salts of hydrochloric and phosphoric acids for pharmacological investigation. Only the hydrochloride and phosphate of the methyl derivative (second carbon atom) were isolated in the crystalline state; they were readily soluble in water. The salts of the phenyl derivative did not dissolve in water, and the salts of the other amides were not obtained in the crystalline form.

TABLE 2

Expt. No.	Formula of the amides	Temperature		Molecular weight of the amide		Nitrogen content (in %)		Notes
		Boiling point of the amide (in °) at pressure (in mm)	Melting point of the amide (in °)	Found	Calculated	Found	Calculated	
1		238 (15)	Does not crystallize	251.3	254	11.12	11.02	Salts not obtained in the crystalline form
2		235-237 (15)	78-80	292.5	296	9.74	9.46	
3		–	94	258.8	254	11.40	11.02	Salts(hydrochloride and phosphate) obtained in the crystalline state
4		–	100-101	270.2	268	10.21	10.44	Salts not obtained in the crystalline form
5		232-234 (13	Does not crystallize	293	296	9.62	9.46	
6		239 (16)		293	296	9.52	9.46	
7		–	176	–	–	9.22	8.86	Salts did not dissolve in water

EXPERIMENTAL

I. Synthesis of Phenamine Derivatives

1. Synthesis of 2-amino-3-phenylheptane (Table 1, No. 4)

α-Butyl-α-phenylacetone was prepared by the alkylation of phenylacetone in the presence of sodium isopropylate. 9.2 g (0.4 mole) of metallic sodium was introduced in small fragments into a solution of 53.6 g (0.4 mole) of phenylacetone and 300 ml of dry isopropyl alcohol. After the formation of the sodium isopropylate, 73.6 g (0.4 mole) of butyl iodide was added in drops. The contents of the flask were heated for 2 hours, the alcohol was distilled off, the residue diluted with water, and the ketone which was evolved was extracted with ether. After distilling off the ether, the ketone was vacuum distilled (15 mm). 25 g of α-butyl-α-phenylacetone was isolated by repeated fractional distillation:

b.p. 116° (15 mm); n_D^{20} 1.50342; d_4^{20} 0.9597; MR_D 58.56. $C_{13}H_{18}O\Gamma_3$; calculated 58.64.

The formyl derivative was prepared by heating 42 g of α-butyl-α-phenylacetone and 50 g of formamide for 16 hours at a temperature of 180-205°.

The following fractions were obtained by vacuum distilling the mixture (13 mm): 1st b.p. 96-114°, 31 g (a stratified liquid consisting of ketone and formamide); 2nd b.p. 114-200°, 5 g; 3rd b.p. 200-203°, 14 g.

The third fraction corresponded to the formyl derivative and was a viscous liquid which crystallized on standing:

b.p. 200-203° (13 mm); n_D^{20} 1.51326; d_4^{20} 0.9922; MR_D 66.39. $C_{14}H_{21}ON\Gamma_3$; calculated 66.86.

0.2280 g sub.: 10.6 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.50. $C_{14}H_{21}ON$. Calculated %: N 6.39.
0.2246 g sub.: 16.76 g benzene: Δt 0.312°. Found: M 220.3. $C_{14}H_{21}ON$. Calculated: M 219.

2-Amino-3-phenylheptane was obtained by the hydrolysis of the formyl derivative (55 g) by energetic boiling with concentrated HCl (100 ml) for 24 hours; the mixture was diluted with water, the unreacted formyl derivative extracted with ether, the amine isolated with solid alkali and extracted with ether. After distilling off the ether, the amine was vacuum distilled. 35 g (73%) of the amine was obtained:

b.p. 114-115° (13 mm); n_D^{20} 1.50675; d_4^{20} 0.9166; MR_D 61.97. $C_{13}H_{21}N\Gamma_3$; calculated 62.06.

0.4000 g sub.: 21.4 ml 0.1 N H_2SO_4 (Kjeldahl). 0.1812 g sub.: 15.11 g benzene: Δt 0.32°. Found %: N 7.49; M 192. $C_{13}H_{21}N$. Calculated %: N 7.32; M 191.

The hydrochloride of 2-amino-3-phenylheptane was prepared by saturating a solution of 35 g of the amine in dry ether with dry gaseous HCl. 40.2 g (96%) of the salt was obtained. A portion of the salt was subjected to fractional recrystallization from benzene. Well formed crystals were isolated —parallelopipeds with a m.p. of 148-149°.

0.1804 g sub.: 7.9 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 15.53. $C_{13}H_{22}NCl$. Calculated %: Cl 15.60.

Another portion of the salt was subjected to fractional crystallization from methyl aclohol with ether. A crystalline substance with a m.p. of 228° was isolated.

0.2018 g sub.: 8.8 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 15.46. $C_{13}H_{22}NCl$. Calculated %: Cl 15.60.

2. Synthesis of 2-amino-3-phenylbutane (Table 1, No. 1)

The synthesis was carried out analogously to that of 2-amino-3-phenylheptane. By fractional crystallization from methyl alcohol with ether, along with the low-melting form of the hydrochloride with a m.p. of 137-138°, a high-melting form was isolated with a m.p. of 212-212.5°.

0.1124 g sub.: 6.05 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 19.08. $C_{10}H_{16}NCl$. Calculated %: Cl 19.13.

3. Synthesis of 2-amino-2,4-dimethyl-1-phenylpentane (Table 1, No. 10)

Formyl derivative. 27.7 g of KCN and 48.6 ml of glacial acetic acid were stirred while being cooled in a three-necked flask supplied with a mechanical stirrer and a reflux condenser. 97.2 g of concentrated H_2SO_4 in 48.6 ml of glacial acetic acid was added in drops to the mixture. The temperature was kept below 20°. 77 g of methylisobutylbenzylcarbinol was added to the reaction mixture. The contents of the flask were heated for 30 minutes on a water bath at a temperature of 70° and left for a day, after which they were poured out into 500 ml of water and neutralized with soda. The oily layer which separated was extracted with ether and the ethereal solution dried with anhydrous Na_2SO_4. After distilling off the ether and distilling the residue in a vacuum, 45 g of a substance in the form of a thick, yellowish oil, which crystallized on standing, was obtained:

m.p. 72-73°, b.p. 210° (15 mm).

0.3018 g sub.: 14.0 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.49. $C_{14}H_{21}ON$. Calculated %: N 6.39.

2-Amino-2,4-dimethyl-1-phenylpentane. 45 g of the formyl derivative was boiled energetically with concentrated HCl (80 ml) for 16 hours. After the usual processing 30 g of the amine was obtained:

b.p. 113-114° (14 mm); n_D^{20} 1.5084; d_4^{20} 0.9219; MR_D 61.77. $C_{13}H_{21}N\ulcorner_3$; calculated 62.06.

0.3310 g sub.: 16.8 ml 0.1 N H_2SO_4 (Kjeldahl). 0.5400 g sub.: 14.40 g benzene: Δt 1.02°. Found %: N 7.10. M 188. $C_{13}H_{21}N$. Calculated %: N 7.32; M 191.

Hydrochloride of the amine. By passing dry gaseous HCl through the ethereal solution, an oil was formed (which did not crystallize).

II. Preparation of the Amides of Nicotinic Acid

A description of the standard method of preparing the amides is set forth below. The properties and analytical data of the amides are set forth in Table 2.

Condensation of 1-phenyl-2-methyl-2-aminopropane with nicotinic acid chloride

A solution of 14.2 g (0.1 mole) of nicotinic acid chloride in 30 ml of benzene was introduced dropwise into a solution of 14.9 g (0.1 mole) of the amine in 30 ml of dry benzene placed in a round bottomed flask supplied with a mechanical stirrer, a reflux condenser and a dropping funnel, after which the mixture was heated for 3 hours at a temperature of 80°. The solution turned brown and the condensation product precipitated in the form of a thick precipitate which was filtered off, washed with benzene, alcohol with ether, and dried. After recrystallization from alcohol, regularly formed, hexagonally shaped crystals with a m.p. of 180° were obtained. The weight was 16 g (55%).

0.1274 g sub.: 4.44 ml 0.1 N $AgNO_3$ (Volhard). Found %: Cl 12.35. $C_{16}H_{19}ON_2Cl$. Calculated %: Cl 12.22.

The hydrochloride dissolved in water, alcohol and chloroform in the cold. The solution of the hydrochloride in water was treated with sodium hydroxide to isolate the free amide; the crystalline substance which separated was filtered off, washed carefully with water and dried. After recrystallization from benzene, regularly formed prismatically shaped crystals were obtained, with a m.p. of 94°.

0.0834 g sub.: 8.0 ml N_2 (16°, 766.8 mm). 0.1400 g sub.: 16.30 g benzene: Δt 0.170°. Found %: N 11.40; M 238.2. $C_{16}H_{18}ON_2$. Calculated %: N 11.02; M 254.

The amide did not dissolve in water. It dissolved in the cold in benzene, ether, acetone, alcohol, chloroform and other organic solvents.

The phosphate was obtained in crystalline form by stirring an alcoholic solution of phosphoric acid (2 moles) with an alcoholic solution of the amide (1 mole) (anhydrous ether was added to initiate the crystallization). After recrystallization from anhydrous ethyl alcohol, the m.p. was 145° and the substance readily dissolved in water.

0.0399 g sub.: 40.15 ml 0.1 N NaOH. Found %: H_3PO_4. 42.90. $C_{16}H_{18}ON_2 \cdot 2H_3PO_4$. Calculated %: H_3PO_4 43.55.

SUMMARY

1. 13 phenamine derivatives with elongated carbon side chains were synthesized. The phenyl derivative appeared to be a more active nervous system stimulant than phenamine.

2. The synthesis and properties of two new phenamine derivatives were described: 2-amino-3-phenylheptane and 2-amino-2,4-dimethyl-1-phenylpentane.

3. The synthesis and properties of seven new amides of nicotinic acid which were of therapeutic significance were described.

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SEVERAL BENZOTHIAZOLE DERIVATIVES

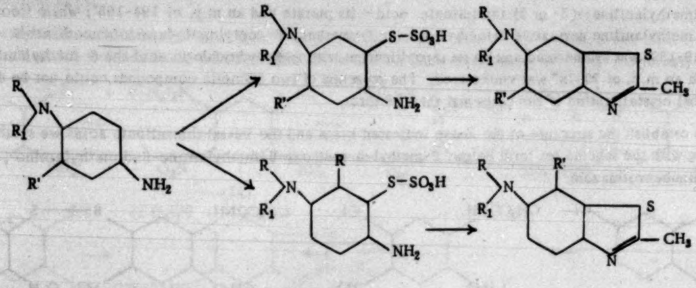
V. SYNTHESIS OF 5-SUBSTITUTED 6-DIMETHYLAMINO-2-METHYLBENZOTHIAZOLES

I. I. Levkoev, N. N. Sveshnikov, I. N. Gorbacheva, N. S. Barvyn and T. V. Krasnova

6-Dialkylamino-2-alkylbenzothiazoles were synthesized for the first time by the action of the acid chlorides or anhydrides of carboxylic acids on p-amino-m-mercaptodialkylanilines or their salts [1, 2]. Later Kiprianov and Sych showed [3] that 2-methyl-6-dialkylaminobenzothiazoles are readily formed by heating the accessible p-aminodialkylaniline-m-thiosulfonic acids with acetic anhydride and acetic acid [4] (cf. also [10]).

It seemed expedient to use this method to obtain 2-methyl-6-mono- and dialkylaminobenzothiazoles, which contained various substituents in the hetero radical, via the conversion of substituted p-aminomono- and dialkylanilines into the corresponding thiosulfonic acids, with subsequent treatment of the latter or their reduction products with acetic anhydride.

In the case of o-substituted p-aminomono- or dialkylanilines it could be expected during their acidification in mixtures with thiosulfates that two isomeric thiosulfonic acids and their corresponding 5- and 7-substituted 2-methyl-6-mono- or dialkylaminobenzothiazoles would be formed



R - alkyl; R_1 - H or alkyl; R' - substituting group

In the present work we investigated the preparation of thiosulfonic acids from o-methoxy-, o-chloro- and o-dimethylamino-p-aminodimethylanilines and o-methoxy-p-aminomethylaniline, and the conversion of these compounds into the corresponding 2-methylbenzothiazoles.

The initial o-methoxy- and o-chloro-p-aminodimethylanilines were prepared from the corresponding 2-substituted dimethylanilines via 4-nitro derivatives. 2-Methoxy-4-aminomethylaniline was synthesized by reduction with excess stannous chloride of 2-methoxy-4-nitrophenylmethylnitrosoamine, which, as had been shown previously [5], is formed during the action of excess nitrous acid on 2-methoxydimethylaniline.

3,4-Bis-(dimethylamino)-aniline, which had not been described up to the present time, was prepared by the reduction of 3,4-bis-(dimethylamino)-nitrobenzene, which could be synthesized in a satisfactory yield by heating 2-chloro-5-nitrodimethylaniline with an alcoholic solution of dimethylamine at 150°.

During the oxidation with potassium dichromate of the p-diamines indicated above in a mixture with sodium thiosulfate in acetic acid solution, the liquid assumed a muddy green color and quickly evolved the corresponding thiosulfonic acids. During the investigation of the compounds obtained the presence of two isomers could not be detected in any case.

The synthesized, substituted p-phenylenediaminethiosulfonic acids were further heated with a mixture of acetic acid and acetic anhydride. However, in contrast to p-aminodimethyl- or diethylaniline-m-thiosulfonic acid [3], the benzothiazole derivatives were formed with small yields and were strongly contaminated with the corresponding tetraaminodiphenyldisulfides.

In connection with this it seemed necessary to convert the thiosulfonic acids obtained into thiophenols. In accord with the literature data, the reduction of similar thiosulfonic acids usually is carried out with zinc powder in acidic medium [1, 2]. To obtain the benzothiazole derivatives the zinc salts of diaminothiophenols were isolated which were then treated with carboxylic acids, their anhydrides or acid chlorides [2].

However, the preparation of pure zinc salts of diaminothiophenols was rather complicated and involved considerable losses, since it was necessary to separate them by fractional precipitation from zinc sulfide and disulfides.

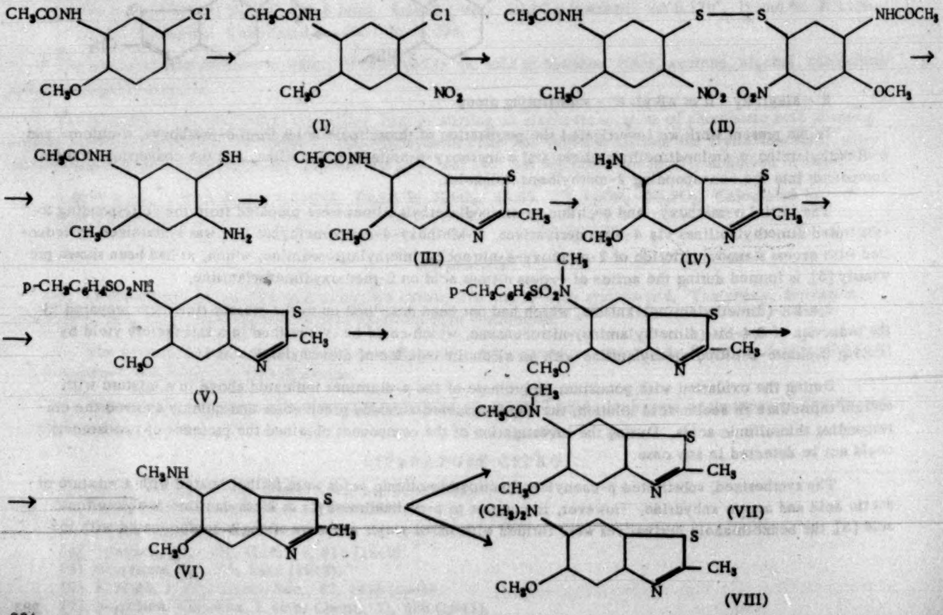
Therefore, taking into account Bemthsen's observations on the formation of p-amino-m-mercaptodimethylaniline during the treatment of the corresponding thiosulfonic acids with ammonium sulfide [6] and the ready closure of the benzothiazole ring by the action of mineral acids on o-acylaminothiophenols [7], we worked out a new method of converting p-phenylenediaminethiosulfonic acids into 6-amino substituted 2-methylbenzothiazoles.

It turned out that such thiosulfonic acids are very readily reduced to diaminothiophenols by sodium sulfide in aqueous or alcoholic solutions. By addition of acetic anhydride to the solution obtained, acetamino derivatives are formed which are smoothly converted into 6-amino substituted 2-methylbenzothiazoles by treatment with hydrochloric acid.

With this method we succeeded in converting all the above-indicated p-phenylenediaminothiosulfonic acids and also the most simple compounds of this series – m-thiosulfonics of p-aminodimethyl- and diethylaniline into derivatives of 2-methylbenzothiazole with excellent yields.

2-Methyl-x(5- or 7)-methoxy-6-dimethylaminobenzothiazole was thereby prepared from 4-amino-2-methoxydimethylaniline-x(3- or 5)-thiosulfonic acid – its picrate had an m.p. of 194-195°; while from the analogous methylaniline derivative 2-methyl-x(5- or 7)-methoxy-6-acetylmethylaminobenzothiazole with an m.p. of 129-130° was synthesized, and by its saponification with 20% hydrochloric acid the 6-methylamino derivative with an m.p. of 77-78° was synthesized. The presence of two isomeric compounds could not be detected by fractional crystallization of the bases and their picrates.

To establish the structure of the above indicated bases and the initial thiosulfonic acids we synthesized, in accordance with the scheme set forth below, 2-methyl-5-methoxy-6-methylamino-6-dimethylamino-, and 6-acetylmethylaminobenzothiazole:



By nitration of 2-methoxy-5-chloroacetanilide in sulfuric acid at 20 - 25°, only the 4-nitro derivative with an m.p. of 191-192° was obtained, which had already been described, without demonstration of its structure, in several patents [8].

Its structure was established via conversion into the diamine, which gave an intensive indamine reaction and was readily converted by oxidation into the recently described 2-chloro-5-methoxy-1,4-benzoquinone [9, 10].

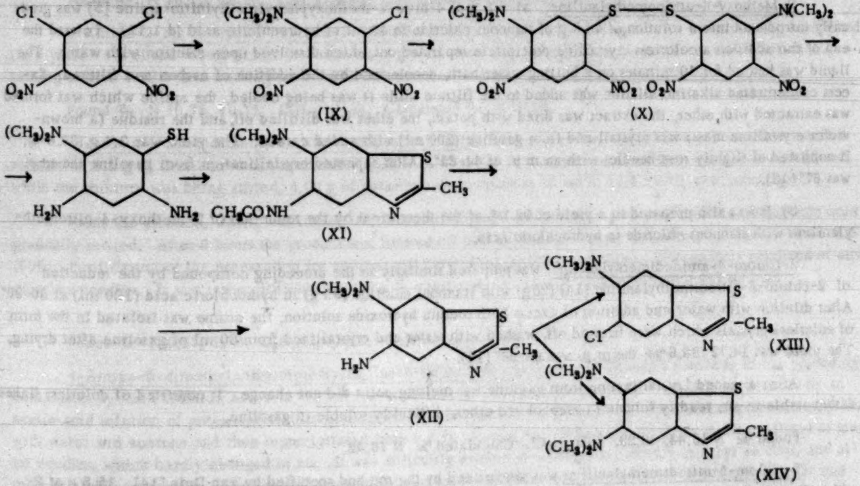
2-Methoxy-4-nitro-5-chloroacetanilide (I) was converted via heating with sodium disulfide into the disulfide (II), which was reduced with zinc powder in acetic acid, and the aminothiophenol salt which was formed was treated with acetic anhydride without isolation; the 2-methyl-5-methoxy-6-acetaminobenzothiazole (III) obtained thereby in excellent yield was saponified with 20% hydrochloric acid, and the amine (IV) was converted by heating with p-toluenesulfochloride in pyridine into the p-tolusulfamino derivative (V).

The latter was then methylated with dimethylsulfate in an aqueous alkali solution and the 2-methyl-5-methoxy-6-methyl-p-tolusulfaminobenzothiazole which precipitated was boiled with hydrochloric acid; 2-methyl-5-methoxy-6-methylaminobenzothiazole (VI) was thereby isolated in the form of colorless crystals with an m.p. 77-78°.

By the acetylation of this compound the acetyl derivative (VII) with an m.p. 129-130° was obtained, while by heating p-toluenesulfonic acid with methyl ether, 2-methyl-5-methoxy-6-dimethylaminobenzothiazole (VIII) was obtained, the picrate of which had m.p. 193-194°.

Compounds VI, VII and VIII were respectively identical with the bases described above obtained from 2-methoxy-4-aminomethyl- and dimethylanilinethiosulfonic acids. Thus, in all these bases the methoxy group is found in position 5 and, consequently the SSO_3H group is located in the para position to the methoxy group in the initial thiosulfonic acids.

2-Methyl-x(5 or 7)-chloro-6-dimethylaminobenzothiazole with m.p. 67-68° was obtained from 2-chloro-4-aminodimethylaniline-x-thiosulfonic acid by reduction with subsequent treatment with acetic anhydride,



while 2-methyl-x(5 or 7)-6-bis-(dimethylamino)-benzothiazole, the picrate of which had a melting point of 170-171°, was respectively obtained from the 2-dimethylamino derivative.

To establish the structure of these compounds we also carried out the synthesis of the corresponding 5-substituted 2-methyl-6-dimethylaminobenzothiazoles (see the scheme above).

4-6-Dinitro-3-dimethylaminochlorobenzene (IX) [11] was converted by the usual method into the disulfide

(X) which was reduced with zinc powder into acetic acid, and the triaminophenol which was formed was treated with acetic anhydride without isolation. The 2-methyl-5-acetamino-6-dimethylaminobenzothiazole (XI), which was thereby obtained in an excellent yield was saponified with 20% hydrochloric acid.

The 2-methyl-5-amino-6-dimethylaminobenzothiazole (XII) which was formed was converted by the Sandmeyer reaction into the 5-chloro derivative (XIII) (colorless crystals with an m.p. 67-68°). The latter proved to be identical with x-chloro-2-methyl-6-dimethylaminobenzothiazole synthes zed from 2-chloro-4-amino-dimethylaniline via the thiosulfonic acids.

Upon the methylation of 2-methyl-5-amino-6-dimethylaminobenzthiazole with the methyl ester of p-toluenesulfonic acid in aqueous solution [cf. 2, 3], 2-methyl-5,6-bis-(dimethylamino)benzothiazole (XIV) was obtained in small yield. The picrate of this compound melted at 169-170° and exhibited no melting point depression in a mixed sample with the picrate of x-6-bis-(dimethylamino)-2-methylbenzothiazole, synthesized from 3,4-bis-(dimethylamino)-aniline-x'-thiosulfonic acid, which demonstrated the position of the dimethylamino and thiosulfo groups in the latter compounds.

Thus, during the oxidation of the 2-substituted 4-aminomethyl- and dimethylanilines in the presence of sodium thiosulfate, the thiosulfonic group enters into the para position to the substitutent in the 2 position in all cases, and the corresponding 5-thiosulfonic acids are formed, which serve as the starting materials for 5-substituted 2-methyl-6-methyl and dimethylaminobenzothiazoles.

EXPERIMENTAL

(Jointly with A. G. Guseva)

2-Methoxy-4-aminodimethylaniline was prepared by the reduction of 2-methoxy-4-nitrodimethylaniline [5] (4.9 g) with stannous chloride (20.3 g) in hydrochloric acid (20 ml) at 90-95°. The yield was 3.98 g (96%) (from benzene). It consisted of colorless needles, which gradually became rose colored in air, with an m.p. of 91-92° [12].

2-Methoxy-4-aminomethylaniline. a) 5.3 g of 4-nitro-2-methoxyphenylmethylnitrosamine [5] was gradually introduced into a solution of 40.6 g of stannous chloride in 40 ml of hydrochloric acid (d 1.19). Toward the end of the addition a colorless crystalline precipitate separated out, which dissolved upon dilution with water. The liquid was heated for 30 minutes on a boiling water bath, decolorized by the addition of carbon and filtered. Excess concentrated alkaline solution was added to the filtrate while it was being cooled, the amine which was formed was extracted with ether, the extract was dried with potash, the ether was distilled off, and the residue (a brown-violet crystalline mass) was crystallized from gasoline (200 ml) with added carbon. The yield was 3.4 g (89.4%). It consisted of slightly rose needles with an m.p. of 64-65°. After repeated crystallization from gasoline the m.p. was 67° [13].

b) It was also prepared in a yield of 92.1% of the theoretical by the reduction of 2-methoxy-4-nitromethylaniline with stannous chloride in hydrochloric acid.

2-Chloro-4-aminodimethylaniline was prepared similarly to the preceding compound by the reduction of 2-chloro-4-nitrodimethylaniline [14] (20 g) with stannous chloride (90 g) in hydrochloric acid (120 ml) at 80-90°. After dilution with water and addition of excess 30% sodium hydroxide solution, the amine was isolated in the form of colorless crystals which were filtered off, washed with water and crystallized from 60 ml of gasoline after drying. The yield was 14.72 (86.6%); the m.p. was 62-63° [15].

After a second crystallization from gasoline its melting point did not change. It consisted of colorless flakes, rather stable in air; readily soluble in alcohol and ether, difficultly soluble in gasoline.

Found %: N 16.44, 16.29. $C_8H_{11}N_2Cl$. Calculated %: N 16.42.

2-Chloro-5-nitrodimethylaniline was synthesized by the method specified by van Duin [14]. 15.5 g of 2-chlorodimethylaniline in 100 ml of sulfuric acid (d 1.84) at 10-15° and with stirring was nitrated with a mixture of 6.9 g of nitric acid (d 1.5) and 30 ml of sulfuric acid (d 1.84). The mass was stirred for 2 hours at 15-20°, poured out onto 600 g of ice, and neutralized with aqueous ammonia. The precipitate which settled out was filtered off, washed with water, and after drying was crystallized from 25 ml of ethyl alcohol. The yield was 16.4 g (82%); the m.p. was 62-63° [14]. It consisted of long yellow needles.

1,2-Bis-(dimethylamino)-4-nitrobenzene was prepared by heating 2-chloro-5-nitrodimethylaniline (15 g) with 33% solution of dimethylamine (41 g) and ethyl alcohol (35 ml) in an autoclave at 150° for 10 hours. After cooling the mass, 700 ml of water was added, the brown precipitate which settled out was filtered off, washed with water, and after drying (weight 12.9-13.2 g) was crystallized from 30 ml of ethyl alcohol. The yield was 11 g (70%); m.p. 59-60°. After two crystallizations from ethyl alcohol it consisted of coarse, orange, rectangular prisms with an m.p. of 62-63°.

Found %: N 19.87, 19.79. $C_{10}H_{15}O_2N_3$. Calculated %: N 20.09.

1,2-Bis-(dimethylamino)-4-aminobenzene was synthesized by the reduction of the preceding compound (10.45 g) with stannous chloride (45 g) in hydrochloric acid (65 ml) at 90°. After heating for 15 minutes on a boiling water bath the liquid was treated with carbon and filtered. The amine was extracted with ether from the almost colorless filtrate after addition of excess concentrated alkali solution. After drying with potash and distilling off the ether, the residue was vacuum distilled.

The yield was 73% of the theoretical; b.p. 130-132° at 9 mm. It consisted of a yellowish oil, which darkened very rapidly in air. It was rather readily soluble in water. In view of the slight stability of the amine, its benzoyl derivative was prepared for analysis. Colorless needles (from ethyl alcohol with an m.p. of 132-133°).

Found %: N 14.96, 14.75. $C_{17}H_{21}ON_3$. Calculated %: N 14.84.

4-Amino-2-methoxydimethylaniline-5-thiosulfonic acid. A solution of 4.9 g of potassium dichromate in 100 ml of 6.5% acetic acid was added over a period of 1 hour at −5° to 0° to a stirred solution of 8.3 g of 2-methoxy-4-aminodimethylaniline and 12.5 g of sodium thiosulfate in 40 ml of 18% acetic acid. After 12 hours the dark green, finely crystalline precipitate which settled out was filtered off and washed with water and acetone, whereupon it became light grey. The yield was 79% of the theoretical. For analysis the preparation was reprecipitated by acetic acid from a 3% soda solution containing sodium sulfide, carefully washed with water and acetone, and dried in a vacuum at 110°. It consisted of almost colorless needles. It was difficultly soluble in water and acetone, rather more readily soluble in ethyl alcohol.

Found %: N 10.12, 10.20. $C_9H_{14}O_4N_2S_2$. Calculated %: N 10.06.

4-Amino-2-methoxymethylaniline-5-thiosulfonic acid was prepared analogously to the preceding compound (in a yield 74% of the theoretical). It consisted of greyish needles. After reprecipitation from soda solution containing sodium sulfite and washing with water and acetone, the preparation obtained was almost colorless.

Found %: N 10.78, 10.71. $C_8H_{12}O_4N_2S_2$. Calculated %: N 10.60.

4-Amino-2-chlorodimethylaniline-5-thiosulfonic acid. 12.5 g of sodium thiosulfate was introduced into a solution of 8.5 g of 2-chloro-4-aminodimethylaniline in 45 ml of 13% acetic acid, and then for 1 hour at 0-5° and while the mixture was being stirred, 4.09 g of potassium dichromate in 40 ml of 10% acetic acid was added.

From the solution, which was tinged with a brownish-green color, a grey precipitate of the thiosulfonic acid gradually settled. After 6 hours the product was filtered off and washed with water and acetone. The yield was 8.5 g (60%). Purification of the preparation for analysis was carried out as indicated above. The product consisted of almost colorless needles. It was rather difficultly soluble in water and alcohol and almost insoluble in acetone.

Found %: N 9.83, 9.78. $C_8H_{11}O_3N_2S_2Cl$. Calculated %: N 9.91.

4-Amino-2-dimethylaminodimethylaniline-5-thiosulfonic acid. It was obtained similarly to the preceding compounds by the oxidation at − 5 to − 7° of 1,2-bis-(dimethylamino)-4-aminobenzene in 20% acetic acid by an acetic acid solution of potassium dichromate in the presence of sodium thiosulfate. The yield of preparation, washed with water and acetone and then reprecipitated from a soda solution, was 68% of the theoretical. It consisted of greyish needles, which hardly changed in air. It was difficultly soluble in water, more readily in ethyl alcohol, and almost insoluble in acetone. For analysis the thiosulfonic acid was additionally crystallized from ethyl alcohol and dried in a vacuum at 100°.

Found %: N 14.51, 14.60. $C_{10}H_{17}O_3N_3S_2$. Calculated %: N 14.42.

2-Methyl-6-dimethylaminobenzothiazole. 7.44 g of 4-aminodimethylanilino-3-thiosulfonic acid [1] was gradually introduced into a solution of 4.2 g of potassium carbonate in 60 ml of water. The mixture was stirred for 10 minutes, and 21.6 g of crystalline sodium sulfide in 30 ml of water was then added to it; a yellow precipitate thereupon settled out, which was rapidly converted into a dark resinous mass. The mixture was heated while being stirred to 75° and the transparent brown solution which formed was cooled to 20°. 3.2 ml of glacial acetic acid, was poured into the liquid and then 9 ml of acetic anhydride was added during energetic stirring for 2-3 minutes at 20-25°. An oil thereupon settled on the walls of the flask which quickly crystallized. The mixture was stirred for 15 minutes more and acidified with 30 ml of hydrochloric acid (d 1.19). The almost-transparent solution which formed was boiled for 5 minutes, cooled and filtered from the insignificant precipitate.

The latter was washed with 20 ml of water which was combined with the basic filtrate. The liquid was rendered alkaline with 30% sodium hydroxide solution, and the base which separated in the form of an oil was extracted with ether. After drying with potash and distilling off the ether the residue (5.78 g) was vacuum distilled. B.p. 192-194° at 22 mm.

Yield 5.2 g (90%); m.p. 63-64°. After crystallization from gasoline it consisted of colorless prisms with an m.p. of 70-71° [2, 3].

The picrate consisted of shiny, bright yellow flakes (from ethyl alcohol). M.p. 174-176°.

2-Methyl-6-diethylaminobenzothiazole, was prepared analogously to the 4-aminodiethylaniline-3-thiosulfonic acid [1] in a yield of 77.2% of the theoretical. It consisted of a colorless, rapidly-yellowing oil. B.p. 189-190° at 16 mm. (According to Kiprianov and Sych [3], 197-205° at 17 mm).

The picrate consisted of fine yellow prisms (from ethyl alcohol). M.p. 163-165°.

2-Methoxy-4-nitro-5-chloroacetanilide. A mixture of 7.62 ml of nitric acid (d 1.4) and 5.7 ml of sulfuric acid (d 1.84) was gradually added at 20-25° to a solution of 20 g of 2-methoxy-5-chloroacetanilide [16] in 45 ml of sulfuric acid (d 1.84) while the mixture was being stirred. The liquid was stirred for 1 hour at 20-25° and poured out onto 150 g of ice. The precipitate was filtered off, washed with water and dried. The yield was 23.7 g (97 %); m.p. 187-188°. It consisted of needles (from ethyl alcohol). M.p. 191-192° [8].

Found %: N 11.27. $C_9H_9O_4N_2Cl$. Calculated %: N 11.45.

2-Methoxy-4-nitro-5-chloroaniline. 2.44 g of 2-methoxy-4-nitro-5-chloroacetanilide was boiled for 1 hour with 75 ml of 25 % hydrochloric acid. After filtration the orange solution was diluted with 75 ml of water, and rendered alkaline with soda. The brown precipitate was filtered off, washed with water and dried. The yield was 1.83 g (90 %); m.p. 129-130°. It consisted of shiny, dark brown prisms (from alcohol). M.p. 130-131° [8].

Found %: N 13.98. $C_7H_7O_3N_2Cl$. Calculated %: N 13.85.

2-Methoxy-5-chloro-1,4-phenylenediamine. 1.01 g of 2-methoxy-4-nitro-5-chloroaniline was dissolved by heating in 30 ml of 60% ethyl alcohol. After adding 3 ml of acetic acid and 6.5 g of zinc powder the mixture was boiled for 1 hour with a reflux condenser and filtered off from the excess zinc powder. The almost colorless precipitate which fell out on cooling was filtered off and washed with 50 % ethyl alcohol. The yield was 0.7 g (81%). After crystallization from benzene it consisted of slightly greyish prisms with an m.p. of 167-168°. It exhibited a clear indamine reaction.

Found %: N 16.32. $C_7H_9ON_2Cl$. Calculated %: N 16.24.

2-Methoxy-5-chloro-1,4-diacetylaminobenzene. A mixture of 0.35 g of 2-methoxy-5-chloro-1,4-phenylenediamine and 1 ml of acetic anhydride was boiled for 15 minutes and the acetic acid was then distilled off and the residue heated for 30 minutes at 250°. After cooling 10 ml of water was added, the precipitate was filtered off, washed with 5 ml of ethyl alcohol and after drying (yield 74% of the theoretical) was twice crystallized from benzene. It consisted of colorless needles with an m.p. of 236-237°.

Found %: N 10.85. $C_{11}H_{13}O_3N_2Cl$. Calculated %: N 10.92.

2-Methoxy-5-chlorobenzoquinone. A solution of 0.22 g of potassium dichromate in 7 ml of water was gradually added to a filtered solution of 0.35 g of 2-methoxy-5-chloro-1,4-phenylenediamine in 10 ml of 10% sulfuric acid at 4-5°. The liquid initially acquired a dark violet, and then a brown color, and a brown precipitate gradually settled out. After 5-6 hours the mass was shaken with ether, the extract dried with sodium sulfate and the ether distilled off. Yellow crystals (0.13 g) with an m.p. of 161-163° were in the residue. After crystallization from benzene yellow prisms with an m.p. of 170-171° [9, 10] were obtained. The substance was readily soluble in ethyl alcohol and ether and difficultly soluble in gasoline.

Found %: Cl 20.37. $C_7H_5O_3Cl$. Calculated %: Cl 20.55.

2,2'-Dinitro-4,4'-dimethoxy-5,5'-diacetylaminodiphenyldisulfide. A solution of sodium disulfide obtained by heating 9 g of crystalline sodium sulfide with 1.2 g of sulfur was gradually added to a boiling solution of 18.34 g of 2-methoxy-4-nitro-5-chloroacetanilide in 250 ml of ethyl alcohol for 2 hours.

The liquid was then boiled for 6 hours with a reflux condenser, the disulfide precipitate was filtered off and washed with alcohol and water. The yield was 8 g (44%); m.p. 283-284°. It consisted of greenish-yellow leaflets (from gasoline). M.p. 284-285°.

Found %: N 11.79. $C_{18}H_{18}O_8N_4S_2$. Calculated %: N 11.61.

2-Methyl-5-methoxy-6-acetylaminobenzothiazole. A mixture of 7.23 g of 2,2'-dinitro-4,4'-dimethoxy-5,5'-diacetylaminodiphenyldisulfide and 11.7 g of zinc powder was gradually introduced while the mixture was being stirred into 80 ml of glacial acetic acid heated to 90-100°.

After completion of the reduction the mass was heated for 15 minutes on a boiling water bath, and 23 ml of acetic anhydride was then added to it, and the heating was continued on an oil bath at 140-150° for 2 hours. After cooling to 70-80° the liquid was diluted with 50 ml of water, heated to boiling, filtered and the precipitate washed with 50 ml of 50% acetic acid. An excess of a 30% alkali solution was added to the cooled filtrate, combined and washed with acetic acid after dilution with 250 ml of water. The crystalline precipitate which settled out was filtered off, washed with water and dried. The yield was 6.45 g (91%); m.p. 203-205°. After crystallization from ethyl alcohol with added activated carbon the base was obtained in the form of colorless needles with an m.p. of 210-211°.

Found %: N 12.04, 12.08. $C_{11}H_{12}O_2N_2S$. Calculated %: N 11.86.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 199-200°.

2-Methyl-5-methoxy-6-aminobenzothiazole was prepared by boiling 2-methyl-5-methoxy-6-acetylaminobenzothiazole (2 g) with 20% hydrochloric acid (20 ml) for 1 hour. After decolorization with activated carbon the solution was rendered alkaline, the precipitate filtered off, washed with water and dried.

The yield was 90% of the theoretical; m.p. 100-102°. It consisted of colorless prisms (from gasoline). M.p. 104-105° (according to [17] m.p. 106°).

Found %: N 14.51, 14.42. $C_9H_{10}ON_2S$. Calculated %: N 14.43.

The picrate consisted of orange prisms (from alcohol) with an m.p. of 207-208°.

2-Methyl-5-methoxy-6-p-toluenesulfaminobenzothiazole. 3.88 g of the preceding compound, 3.85 g of p-toluenesulfochloride and 16 ml of pyridine were heated for 1 hour on a boiling water bath.

The yellowish solution was diluted with 200 ml of water and neutralized with hydrochloric acid; the precipitate which settled out was filtered off, washed with water and dried. The yield was 98.8% of the theoretical. M.p. 138-139°. After two-fold crystallization from ethyl alcohol it consisted of colorless needles with an m.p. of 147-148°; it was rather readily soluble in ethyl alcohol, and difficultly soluble in gasoline.

Found %: N 7.89. $C_{16}H_{16}O_3N_2S_2$. Calculated %: N 8.05.

The picrate consisted of yellow prisms (from alcohol). M.p. 175-176°.

Found %: N 12.09. $C_{22}H_{19}O_{11}N_5S_2$. Calculated %: N 12.13.

2-Methyl-5-methoxy-6-N-methyl-p-toluenesulfaminobenzothiazole. 1.9 g of dimethylsulfate was added to a filtered solution of 1.75 g of 2-methyl-5-methoxy-6-p-toluenesulfaminobenzothiazole and 0.8 g of sodium hydroxide in 40 ml of water, and the mixture was shaken for 30 minutes. A yellow oil thereupon separated which quickly crystallized. A solution of 0.6 g of sodium hydroxide in 10 ml of water was then added and the mixture was heated for 30 minutes at 70-75°. After cooling the precipitate was filtered off and washed with water. The yield was 1.6 g (88%). The m.p. was 143-145°. It consisted of slightly yellowish prisms (from gasoline). M.p. 148-149°. It was readily soluble in ethyl alcohol and rather difficultly soluble in gasoline.

Found %: N 7.91. $C_{17}H_{18}O_3N_2S_2$. Calculated %: N 7.73.

The picrate consisted of yellow prisms (from alcohol). M.p. 154-155°.

2-Methyl-5-methoxy-6-methylaminobenzothiazole. a) 1.81 g of the preceding compound was boiled for 4 hours with 20 ml of hydrochloric acid (d 1.17). The solution was then diluted with 100 ml of water, rendered alkaline, and the precipitate which settled out was filtered off and washed with water. The yield was 0.8 g (77%). The m.p. was 73°. After two crystallizations from gasoline it consisted of shiny, yellowish needles with an m.p. of 77-78°. It was very readily soluble in ethyl alcohol and somewhat more difficultly soluble in gasoline.

Found %: N 13.30, 13.42. $C_{10}H_{12}ON_2S$. Calculated %: N 13.46.

The picrate consisted of orange prisms (from alcohol). M.p. 217-218°.

b) 0.5 g of 2-methyl-5-methoxy-6-methylacetylaminobenzothiazole (see below) was boiled for 2 hours with 10 ml of 20% hydrochloric acid. The solution was treated with carbon, rendered alkaline and the base which was formed was extracted with ether. After distilling off the ether the residue weighed 0.37 g (88.9%); m.p. 67-68°. After two-fold crystallization from gasoline the m.p. was 76-77°. It yielded no melting point depression in a mixed sample with the preparation obtained by method (a).

2-Methyl-5-methoxy-6-methylacetylaminobenzothiazole. a) 1.53 g of 4-amino-2-methoxymethylaniline-5-thiosulfonic acid was dissolved at 30-40° in a solution of 0.7 g of potassium carbonate in 5 ml of water, and 2.4 g of crystalline sodium sulfide in 3 ml of water was added to the liquid over a period of 2-3 minutes while it was being stirred. A yellow precipitate thereupon settled out which then almost completely dissolved. After decolorization with activated carbon 14 ml of ethyl alcohol and 1.55 g of acetic anhydride was added to the solution. After 12 hours, the ethyl alcohol and the ethyl acetate were distilled off from the liquid after it had been acidified with hydrochloric acid and the base was liberated by alkalinization and extracted with ether. The extract was dried with potash, the ether distilled off and the residue crystallized from gasoline with added carbon. The yield was 3.9 g (67%). It consisted of slightly yellowish prisms with a m.p. of 127-128°.

b) A mixture of 0.1 g of 2-methyl-5-methoxy-6-methylaminobenzothiazole (with an m.p. of 73°) and 0.1 g of acetic anhydride was heated for 2 hours at 115° and after cooling was diluted with 2 ml of water and rendered alkaline with potash. The precipitate which settled out was filtered off and washed with water. The yield was 0.07 g (56%); m.p. 127-128°. A mixed sample of the preparations obtained by both methods melted at 127-128°. After crystallization from gasoline the base was obtained in the form of colorless prisms with an m.p. of 129-130° which did not change during repeated purification. It was rather difficultly soluble in gasoline and readily soluble in ethyl alcohol, ether and acetone.

Found %: N 11.34. $C_{12}H_{14}O_2N_2S$. Calculated %: N 11.20.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 172-173°.

Found %: N 14.76. $C_{18}H_{17}O_9N_5S$. Calculated %: N 14.61.

2-Methyl-5-methoxy-6-dimethylaminobenzothiazole. a) 5.56 g of 2-methoxy-4-aminodimethylaniline-5-thiosulfonic acid was dissolved at 30-40° in a solution of 2.8 g of potassium carbonate in 40 ml of water, and 14.4 g of crystalline sodium sulfide in 20 ml of water was added to the liquid over a period of 2-3 minutes while the mixture was being stirred; a yellow precipitate thereupon settled out which then almost completely dissolved. The liquid was heated to 60°, filtered from the insignificant dark precipitate, and 4.8 ml of glacial acetic acid and, during stirring, 6 ml of acetic anhydride was added to the filtrate after it had been cooled to 15°. An oil thereupon settled out which rapidly crystallized. The mixture was stirred for 15 minutes more, acidified with 20 ml of hydrochloric acid (d 1.17), heated for 30 minutes on a boiling water bath, and then boiled for 5 minutes and filtered from the sulfur and other admixtures. The slightly greenish filtrate was rendered alkaline with a 30% sodium hydroxide solution while being cooled; a greenish oil thereupon settled out which gradually crystallized. The base was extracted with ether, and the ether was distilled off after drying with potash and the residue was heated for 30 minutes in a vacuum on a boiling water bath. The yield was 4.0 g (90%); m.p. 55-57°. After crystallization from gasoline 3.7 g with an m.p. of 58-59° was collected. After a second crystallization from gasoline the melting point of the preparation was raised to 59-60° and it did not change during additional purification. It consisted of colorless prisms; the base was very readily soluble in alcohol, ether and benzene and somewhat more difficultly soluble in gasoline.

Found %: N 12.82, 12.84. $C_{11}H_{14}ON_2S$. Calculated %: N 12.61.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 194-195°.

Found %: N 15.60, 15.68. $C_{17}H_{17}O_8N_5S$. Calculated %: N 15.52.

b) A mixture of 0.21 g of 2-methyl-5-methoxy-6-methylaminobenzothiazole and 0.4 g of the methyl ester of p-toluenesulfonic acid was heated for 15 minutes on a boiling water bath. The thick brownish mass which formed was dissolved in 10 ml of soda, and the solution was filtered off from the insignificant colorless precipitate, which was washed with water and dried.

The weight was 0.08 g; m.p. 73-75°. No melting point depression was displayed in a mixed sample with 2-methyl-5-methoxy-6-methylaminobenzothiazole.

The aqueous solution was shaken with ether and then neutralized with sodium bicarbonate; a yellowish oil was thereupon evolved which was extracted with ether. After drying with potash the ether was distilled off, the residue (0.06 g) entirely crystallized on cooling; m.p. 52-57°. After crystallization from gasoline the product (0.04 g) was converted into the picrate (weight 0.06 g, m.p. 186-190°), which was purified by two-fold crystallization from ethyl alcohol. The weight was 0.03 g; m.p. 193-194°. No melting point depression was displayed in a mixed sample with the picrate of the 2-methyl-5-methoxy-6-dimethylaminobenzothiazole prepared by method (a).

A considerable quantity of quaternary salt was isolated from the aqueous solution after extraction of the base; on heating with ethyl orthoformate in pyridine these salts formed carbocyanine with an absorption maximum at 600 mμ (in alcohol).

4,6-Dinitro-1,3-dichlorobenzene was obtained by the nitration of 1,3-dichlorobenzene (synthesized by the Sandmeyer reaction from m-phenylenediamine [18] or m-chloroaniline [19] with respective yields of 70% and 73% of the theoretical) with a mixture of sulfuric acid and potassium nitrate at ordinary temperatures [20]. The yield of purified product with an m.p. of 101-102° [20] amounted to 65% of the theoretical.

4,6-Dinitro-3-dimethylaminochlorobenzene. A mixture of 23.7 g of 4,6-dinitro-1,3-dichlorobenzene, 13 g of a 33% aqueous solution of dimethylamine, 13 g of crystalline sodium acetate and 230 ml of ethyl alcohol was boiled for 3 hours in a flask with a reflux condenser. After cooling, the precipitate was filtered off and washed with alcohol, water and ether. The yield was 22.2 g (90.5%); m.p. 125°. After crystallization from 300 ml of ethyl alcohol it consisted of shiny yellow needles (19.1 g) with an m.p. of 129° [11].

2,2',4,4'-Tetranitro-5,5'-bis(dimethylamino)diphenyldisulfide. A solution of sodium disulfide obtained by heating 1.3 g of 60% sodium sulfide and 0.5 g of sulfur in 60 ml of alcohol was gradually added over a period of one hour to a boiling solution of 4.91 g of 4,6-dinitro-3-dimethylaminochlorobenzene in 150 ml of ethyl alcohol.

The liquid was then boiled for 30 minutes with a reflux condenser, the yellow precipitate of disulfide which settled out after cooling was filtered off and washed with water and alcohol. The yield was 4.52 g (93%); m.p. 210-212°. For analysis the preparation was crystallized from alcohol, and then from benzene. It consisted of shiny yellow flakes (from benzene). M.p. 216°. It was difficultly soluble in ethyl alcohol and somewhat more readily soluble in benzene.

Found %: N 18.90, 18.94; S 13.45. $C_{16}H_{16}O_8N_6S_2$. Calculated %: N 18.75; S 13.24.

2-Methyl-5-acetylamino-6-dimethylaminobenzothiazole. A mixture of 4.84 g of 2,2',4,4'-tetranitro-5,5'-bis(dimethylamino)diphenyldisulfide and 31.1 g of zinc powder was gradually introduced into 50 ml of glacial acetic acid heated to 80-90° and stirred.

After completion of the reduction the thick greyish-white reaction mass was heated for 15 minutes on a boiling water bath, and 6.1 g of acetic anhydride was then added to it and the mixture was boiled for 30 minutes. After cooling to 70-80° the liquid was diluted with 60 ml of water, acidified with hydrochloric acid to an acid reaction as registered by Congo red (45 ml of hydrochloric acid, d 1.18), heated to boiling and filtered from admixtures. The filtrate, while being cooled, was rendered alkaline with a 40% sodium hydroxide solution and shaken with ether. The ether was distilled off from the extract to a volume of 7-10 ml after drying with potash, the precipitate which settled out was filtered off and washed with 2-3 ml of ether. The yield was 3.93 g (76%). It consisted of almost colorless prisms (from gasoline). The m.p. was 123°. It was readily soluble in alcohol and ether, and more difficultly soluble in gasoline.

Found %: N 17.03, 16.88. $C_{12}H_{15}ON_3S$. Calculated %: N 16.86.

The picrate consisted of yellow crystals (from alcohol) with an m.p. 155-156°.

Found %: N 17.44. $C_{18}H_{18}O_8N_6S$. Calculated %: N 17.57.

2-Methyl-5-amino-6-dimethylaminobenzothiazole. 2.49 g of 2-methyl-5-acetylamino-6-dimethylaminobenzothiazole was boiled for 2 hours in a flask with a reflux condenser with 7 ml of hydrochloric acid (d 1.19). The almost colorless solution was diluted with 20 ml of water, and after it had been rendered alkaline, was shaken with ether. After drying the extract with potash and distilling off the ether, greyish crystals were left with an m.p. of 88-92°. The yield was 2.05 g (99%).

After crystallization from 30 ml of gasoline 1.33 g with an m.p. of 97-98° was collected. For analysis the preparation was crystallized 2 times more from gasoline. It consisted of yellowish prisms with an m.p. of 100-101°.

Found %: N 20.36, 20.18. $C_{10}H_{13}N_3S$. Calculated %: N 20.08.

The picrate consisted of orange prisms (from alcohol) with an m.p. of 189.5-190°.

Found %: N 19.39. $C_{16}H_{16}O_7N_6S$. Calculated %: N 19.26.

2-Methyl-5-chloro-6-dimethylaminobenzothiazole. a) A solution of 15 g of crystalline sodium sulfide in 15 ml of water was gradually added to a stirred solution of 7.05 g of 4-amino-2-chlorodimethylaniline-5-thiosulfonic acid and 4.25 g of potassium carbonate in 30 ml of water, and the liquid was heated for 10 minutes on a boiling water bath. After separation of an insignificant yellow precipitate, the solution was stirred with 10 ml of ethyl alcohol and 6 ml of acetic anhydride. On the following day the precipitate of sulfur which settled out was filtered off, the filtrate acidified with hydrochloric acid, and after distilling off the alcohol and the ethyl acetate, base was liberated by alkalinization and was extracted with ether. After drying with potash and distilling off the ether the residue (3.34 g) was converted into the picrate (yield 6.21 g; m.p. 197-198°), which was crystallized from ethyl alcohol (m.p. after crystallization 200-201°). The base which was evolved by treatment with soda solution was vacuum distilled (b.p. 170-171° at 12 mm). The yield was 2.75 g (40%); m.p. 64-66°. It consisted of almost colorless flakes (from gasoline with a m.p. of 67-68°. The base was readily soluble in ethyl alcohol and ether, and somewhat more difficultly soluble in gasoline.

Found %: N 12.20, 12.31. $C_{10}H_{11}N_2SCl$. Calculated %: N 12.36.

b) A solution of 1.03 g of 2-methyl-5-amino-6-dimethylaminobenzothiazole in 12 ml of 10% hydrochloric acid was diazotized at 0° with 0.35 g of sodium nitrite in 2 ml of water. The orange solution of diazonium salt obtained was introduced into a solution of 0.62 g of cuprous chloride and 4 ml of hydrochloric acid (d 1.19), whereupon vigorous evolution of nitrogen occurred. The liquid was diluted with 20 ml of water, filtered from the insignificant precipitate, rendered alkaline, and the base which was evolved was extracted with ether. After distilling off the ether the residue was converted into the picrate, which was crystallized from ethyl alcohol.

The yield was 1.2 g; m.p. 200-201°. 0.3 g of base was isolated by decomposition of the picrate, and after crystallization from gasoline the base melted at 67-68°.

Found %: N 12.41. $C_{10}H_{11}N_2SCl$. Calculated %: N 12.36.

A mixed sample of the bases obtained by both methods and also from the picrates displayed no melting point depression.

The picrate was crystallized from ethyl alcohol for analysis. It consisted of yellow needles with an m.p. of 200-201°.

Found %: N 15.17, 15.19. $C_{16}H_{14}O_7N_5SCl$. Calculated %: N 15.37.

2-Methyl-5,6-bis(dimethylamino)benzothiazole. a) It was obtained analogously to the 5-chloro-6-dimethylamino derivative by the reduction of 4-amino-2-dimethylaminodimethylaniline-5-thiosulfonic acid with sodium sulfide with subsequent treatment of the mercaptide solution obtained with acetic anhydride, in the presence of ethyl alcohol and with acidification with hydrochloric acid. The yield of picrate was 75% of the theoretical. The isolated base was purified by vacuum distillation. B.p. 156-157° at 11 mm. It consisted of a yellowish oil which rapidly darkened in air.

The picrate consisted of yellow prisms (from alcohol) with an m.p. of 170-171°.

Found %: C 46.56; H 4.52; N 17.90. $C_{17}H_{20}O_7N_6S$. Calculated %: C 46.75, H 4.52, N 18.10.

b) 0.42 g of 2-methyl-5-amino-6-dimethylaminobenzothiazole and 1.12 g of the methyl ester of p-toluenesulfonic acid were heated for 20 minutes on a boiling water bath while being shaken with a solution of 0.32 g of sodium carbonate in 5 ml of water. The slightly turbid yellowish solution was rendered weakly alkaline with soda after filtration and the oil which was evolved was extracted with ether. After drying with potash the ether was driven off and the residue (0.12 g) was converted into the picrate (weight 0.18 g; m.p. 164-168°). It consisted of yellow prisms (from alcohol) with an m.p. of 169-170°. No melting point depression was displayed in a mixed sample with the picrate of the 2-methyl-5,6-bis(dimethylamino)benzothiazole obtained by method (a).

SUMMARY

1. The oxidation by potassium dichromate of a number of 2-substituted 4-aminomethyl- and dimethylanilines in the presence of sodium thiosulfate was investigated. It was shown that the corresponding 5-thiosulfonic acids are thereby smoothly obtained.

2. A new general method of converting p-phenylenediaminothiosulfonic acids into 6-amino derivatives of 2-methylbenzothiazole was worked out.

3. The synthesis of a number of 5-substituted 6-dimethylamino-2-methylbenzothiazoles and also of the corresponding 6-amino- and 6-methylamino-5-methoxy derivatives was carried out.

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* See Consultants Bureau Translation, page 1217.

** See Consultants Bureau Translation, page 307 and 313 ff.

SUMMARY

4. The oxidation of [illegible] of a [illegible] in the presence of [illegible], and [illegible] are thereby smoothly obtained.

5. A new general method of [illegible] was worked out.

6. The [illegible] and [illegible]

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INVESTIGATION OF THE REDUCTION OF γ-DINITRILES BY VYSHNEGRADSKY'S METHOD

A. P. Terentyev and V. G. Yashunsky

The reduction of nitriles by Vyshnegradsky's method with sodium in alcohol under various conditions can be successfully used for the synthesis of several difficultly-obtainable cyclic nitrogenous bases [1, 2, 3, 4].

Cyclization can occur in the case of reduction of nitriles on which, along with the nitrile group, there is another nitrile group, a primary amine group, or a keto group, as a rule in the β- or γ-position.

The formation of cyclic imines during the reduction of nitriles by succinic and glutaric acids was detected for the first time by Ladenburg [5], who, however, did not establish the quantitative ratios between the linear and cyclic products thereby obtained. The formation of ammonia and volatile bases was also observed by other authors during the reduction of 1,2- and 1,3-dinitriles [6, 7].

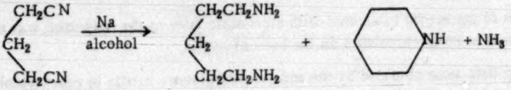
Korshak and Rafikov [8] found that during the reduction of nitrile by adipic acid, a small quantity of α-ethylpyrrolidine was formed along with the hexamethylenediamine.

In spite of the large amount of data concerning the formation of cyclic imines during the reduction of nitriles by sodium in alcohol, up to the present time no systematic study of the conditions and factors which influence the cyclization process or the mechanism of this reaction has been carried out. Apparently, this is due to the difficulty of separating and determining amines under these conditions.

We undertook a detailed study of this reaction in the simplest example – the nitrile of glutaric acid, using the analytical method of investigating the end products without isolating them.

About 1 g (approximately 0.01 mole) of the dinitrile and 3.2 g of metallic sodium were taken for each experiment. Thus, in all the experiments approximately one mole of hydrogen, formed due to the reaction of sodium with alcohol, was available per mole of nitrile.

The reduction of glutaronitrile leads to the following products:



In addition, some ammonia can be formed due to the partial saponification of the nitrile.

Secondary linear amines ($H_2N-(CH_2)_5-NH-(CH_2)_5-NH_2$) are practically not formed under these conditions.

The method of analysis, worked out on the basis of the work of Mizuch and Isavchenko [9], consisted of the determination of ammonia via its precipitation in the form of the complex with sodium cobaltinitrite, while pentamethylenediamine was precipitated with the aid of the nitrite method of Van Slyke in a modified Ioanisiani [10] microdetermination apparatus. The quantity of piperidine was found as the difference between the total amine nitrogen determined by titration of the reaction products and the nitrogen of the diamine and ammonia. The method was verified on several artificial mixtures of these three components and manifested a precision to ±0.5%.

The experiment (No. 1) involving the reduction of the nitrile of glutaric acid with sodium in absolute ethyl alcohol at a molar ratio of the reacting components nitrile : alcohol : sodium = 1:95:15 was taken as the standard for comparison. The total yield of diamine and piperidine amounted to 77% (calculating on the basis of nitrile taken) under these conditions, while the molar ratio of the first and second was equal to 4:1.

It was found that the duration of the reaction appreciably influenced the yields of linear and cyclic amines: the slower the reaction proceeded, the greater the extent to which piperidine was formed. The quantity of diamine obtained was also thereby increased; however, very prolonged reduction lowered its yield. Thus, the time of reaction is a dependent variable and can be regulated by the reaction temperature, the method of introducing sodium and the quantity of alcohol, while the determining factor here, apparently, is the rate of solution of sodium in alcohol, i.e., the intensity of hydrogen formation.

Our experiments showed that a less energetically proceeding reaction of sodium with alcohol facilitates cyclization under the given conditions. Therefore, the increase in the quantity of alcohol for reduction, which accelerates the solution of the sodium, leads to diminished yields of diamine, and particularly of piperidine (Fig. 1).

Diminished nitrile concentration due to addition of inert solvents to the alcohol, as one would expect, favorably influences the course of cyclization and negatively influences the formation of diamine; the total yield of both amines remains almost the same (Fig. 2).

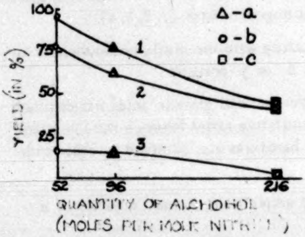


Fig. 1. The yield of reaction products as a function of the quantity of alcohol. 1) Total yield; 2) yield of diamine; 3) yield of piperidine. Experiment numbers: a) 1; b) 3; c) 4.

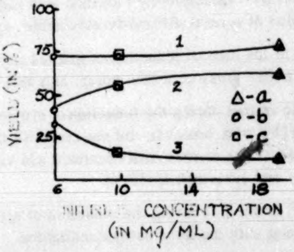


Fig. 2. Yield of reaction products as a function of the nitrile concentration. 1) Total yield; 2) yield of diamine; 3) yield of piperidine. Experiment numbers: a) 1; b) 8; c) 9.

The addition to the reaction mixture of nickel formate (0.3 g) which was reduced to metallic nickel, almost tripled the ratio of linear and cyclic reaction products in the direction of diamine – 11:1 (in the standard experiment it was equal to 4:1). Apparently in the presence of this catalyst a portion of the uselessly evolved molecular hydrogen also participates in the reduction of the nitrile.

The use of an alloy of sodium with potassium (2% K) for the reduction, as one should expect [11], increased the yield of both products; the total amine yield reached 93%, calculated on the basis of the nitrile.

The reduction was carried out with finely divided sodium with the object of elucidating the influence of the metal surface on the course of the reaction; there was no substantial difference in the results in comparison with the standard conditions.

Treatment of the nitrile in alcohol with alcoholate prior to the reduction was reflected only in an increase of the diamine yield to 80%, calculated on the basis of nitrile.

Interesting data were obtained by the reduction of glutaric nitrile in other alcohols – methyl, butyl and cyclohexyl (Table 1; about 50 ml of alcohol was taken in all experiments). An increase in the yields of diamine and piperidine was detected from methyl alcohol to ethyl and butyl alcohols. As a result of the reduction of nitrile in cyclohexyl alcohol it was shown that piperidine is formed in twice as large a quantity as the diamine with a total amine yield of 91%. In the given case, apparently, the high reaction temperature (165°) plays a decisive role.

Thus, as a result of the study of the reduction of glutaric nitrile by sodium in alcohol, it was established that increasing the duration of the reaction, decreasing the nitrile concentration, and increasing the reaction temperature facilitate the course of the cyclization process with formation of piperidine

In order to elucidate the influence of substitutents in the *a*-position of glutaric nitrile on the degree of formation of cyclic products in this reaction, we carried out the reduction of the dinitriles of *a*-methyl and *a*-phenylglutaric acids under standard conditions. It was found that both substituted nitriles give much higher yields of cyclic imines (Table 2).

With the object of studying the cyclization mechanism during the reduction of dinitriles by the Vyshnegradsky method, we treated pentamethylenediamine with sodium in alcohol under standard conditions. The formation of appreciable quantities of ammonia was not detected under these conditions. Our results confirmed the previously

TABLE 1

Reduction of Glutaric Acid Nitrile in Various Alcohols

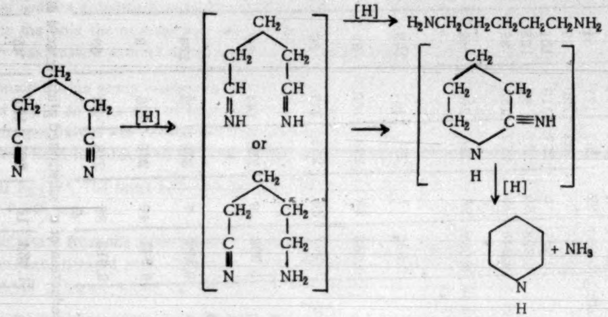
Expt. No.	Alcohol				Ratio diamine/piperidine
		Diamine	Piperidine	Total	
12	Methyl	27.0	9.0	36.0	3/1
1	Ethyl	61.5	15.5	77.0	4/1
13	n-Butyl	80.0	18.5	98.5	4.3/1
14	Cyclohexyl	30.0	61.0	91.0	1/2

TABLE 2

Reduction of Dinitriles of Glutaric Acids in Ethyl Alcohol

Expt. No.	Acid Nitriles	Yield of products (in moles %)			Ratio A/B	Yield of products according to the literature data.		
		Diamine (A)	Cyclic product (B)	Total		Diamine	Cyclic product	Reference
1	Glutaric	61.5	15.5	77.0	4/1	80**	–	[5]
15	*a*-Methylglutaric	68.5	21.0	89.5	3/1	47	23	[7]
16	*a*-Phenylglutaric	34.5*	34.0	68.5	1/1	–	59***	[1]

proposed hypothesis [5] concerning the possibility of the formation of piperidine in this reaction due to the cleavage of ammonia from the diamine. It could therefore be expected that the process of the reduction of glutaric acid nitrile by sodium in alcohol proceeds according to the following scheme (just as was established in the case of the catalytic hydrogenation [12]): first stage – formation of intermediate diamine or aminonitrile, then either further hydrogenation to diamine or cyclization into piperidonimine (amidine), which is readily converted by the action of sodium in alcohol [12] into piperidine with the evolution of ammonia



Apparently the slowest of these reactions is the direct cyclization – the establishment of the C–N bond. Consequently increased duration and increased temperature favor its passage

Decreased nitrile concentration also exerts a positive influence on the formation of piperidine, slowing the hydrogenation of the intermediate products to diamine.

If our hypothesis concerning the mechanism of cyclization is correct, then one can expect that the mechanism of the reduction of nitriles by Vyshnegradsky's reaction is in general the same as during their catalytic hydrogenation [13], i.e., the intermediate stage appears to be an imine.

EXPERIMENTAL

The dinitrile of glutaric acid was prepared from 1,3-dibromopropane [14], b.p. 110-112° at 3 mm, n_D^{25} 1.4330, d_4^{25} 0.9825, MR_D 24.89, calculated 24.93. the literature data: b.p. 131-134° at 10 mm [14].

The dinitrile of *a*-methylglutaric acid was prepared by an analogous method from 1,3-dibromobutane b.p. 137-138° at 14 mm, n_D^{25} 1.4320; d_4^{25} 0.9512; MR_D 29.49, calculated 29.55. Literature data: b.p. 134°

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* The low yield of diamine is apparently to be explained by the fact that it could not be entirely distilled off from the reaction products.

** The yield is given for the hydrochloride.

*** The reduction was carried out in butyl alcohol.

TABLE 3
Reduction of Glutaric Acid Dinitrile

Expt. No.	Alcohol	Reaction conditions	Nitrile (in g)	Duration (min)	N found (in mg)				Obtained (moles)			Yield (mole %)			Ratio diamine:piperidine (moles)
					in distillate	of diamine	of ammonia	of piperidine	of diamine	of piperidine	of nitrile	diamine	piperidine	total	
1	Ethyl 50 ml	Addi. of nitrile sol. to Na, heating	0.950	15	274	174	78	22	0.00622	0.00157	0.01010	61.5	15.5	77.0	4:1
2	Ethyl 50 ml	Intro. of Na to nitrile sol. heating	0.896	22	253	171	51	26	0.00630	0.00186	0.00953	66.0	19.5	85.5	3.4:1
3	Ethyl 30 ml	As in Experiment 1	0.940	28	262	220	19	23	0.00786	0.00164	0.01000	78.5	16.5	95.0	5:1
4	Ethyl 120 ml	As in Experiment 1	0.911	6	267	113	151	3	0.00403	0.00021	0.00970	41.5	2.0	43.5	20:1
5	Ethyl 50 ml	Cooling to 20°	0.898	60	262	95	125	42	0.00339	0.00300	0.00954	35.5	31.5	67.0	1:1
6	Ethyl 50 ml	As in Expt. 1. Addi. of 0.3 g of nickel formate	0.940	18	273	183	82	8	0.00654	0.00057	0.01000	65.5	6.0	71.5	11:1
7	Ethyl 50 ml	Addition of the nitrile solution to an alloy of Na and K (K 0.07 g), heating	0.962	28	280	208	43	29	0.00743	0.00207	0.01020	73.0	20.0	93.0	3.5:1
8	Ethyl 50 ml; toluene 100 ml	As in Experiment 1	0.898	7	261	111	108	42	0.00396	0.00300	0.00954	41.5	31.5	73.0	1.3:1
9	Ethyl 50 ml; dioxane 50 ml	As in Experiment 1	0.968	13	274	160	89	25	0.00572	0.00179	0.01030	55.5	17.5	73.0	3:1
10	Ethyl 50 ml	As in Experiment 2; heating for 10 minutes with 1.4 g $NaOC_2H_5$ before the reaction	0.907	23	256	217	20	19	0.00775	0.00136	0.00965	80.0	14.0	94.0	5.7:1
11	Ethyl 50 ml; toluene 15 ml	Addition of the nitrile solution to finely divided Na while the mixture was being stirred	0.902	6	258	144	92	22	0.00515	0.00157	0.00960	54.0	16.0	70.0	3.4:1
12	Methyl 50 ml	As in Experiment 1; Temperature 70°	0.892	7	258	72	174	12	0.00257	0.00086	0.00950	27.0	9.0	36.0	3:1
13	n-butyl 50 ml	As in Experiment 2; Temperature 120°	0.947	40	260	226	8	26	0.00807	0.00186	0.01010	80.0	18.5	98.5	4.3:1
14	Cyclohexyl 50	As in Experiment 2; Temperature 165°	0.913	35	218	82	53	83	0.00294	0.00592	0.00970	30.0	61.0	91.0	1:2
		Reduction of α-substituted glutaric acid dinitriles													
15	α-Methylglutaronitrile; ethyl 50 ml	As in Experiment 1	1.084	16	266	192	45	29	0.00685	0.00207	0.01000	68.5	21.0	89.5	3:1
16	α-Phenylglutaronitrile; ethyl 50 ml	As in Experiment 1	1.648	17	240	94	100	46	0.00336	0.00328	0.00968	34.5	34.0	68.5	1:1

at 13 mm [7].

The dinitrile of α-phenylglutaric acid was synthesized from benzyl cyanide and acrylonitrile [1], b.p. 155-156° at 3 mm, n_D^{20} 1.5250. Literature data: b.p. 181-183° at 8.5 mm, n_D^{25} 1.5237 [1].

Pentamethylenediamine was prepared by the reduction of the dinitrile of glutaric acid by sodium in butyl alcohol, b.p. 178-179.5°. Literature data: b.p. 178-180° [15].

Reduction of Glutaric Acid Nitrile in Ethyl Alcohol (Standard Experiment No. 1)

3.2 g of metallic sodium was placed in a 100 ml three-necked flask supplied with a dropping funnel and a reflux condenser to which was joined a Tishchenko flask with 10 ml of 0.25 N HCl. A solution of 0.950 g (0.0101 mole) of glutaric acid nitrile in 50 ml of absolute ethyl alcohol was rapidly added from a dropping funnel. The flask was heated on a boiling water bath. After all the sodium had reacted (15 minutes),30 ml of water was poured in.

After cooling, the mixture was transferred to a round-bottom flask with a long neck and, after it had been supplied with a Kjeldahl drop trap, the alkaline solution was subjected to distillation with steam heated to 150°. The distillate was collected in a flask with 74.7 ml of 0.25 N HCl (the end of the adapter was placed below the surface of the liquid in the receiving flask). The end of the distillation was determined by the absence of an alkaline reaction with litmus (about 3 hours. The contents of the Tishchenko flask were then poured off into the distillate and the excess acid in it was titrated with alkali with methyl red as the indicator. 15.9 ml of 0.1 N NaOH was consumed in the titration. The titrated solution was acidified and concentrated on a water bath to a volume of about 30 ml and transferred to a 50 ml measuring flask. 3 ml of a 10% sodium acetate solution and 10 ml of dioxane were added to 10 ml of the solution from the measuring flask. A cooled solution of 1.5 g of the binary salt of sodium cobaltinitrite in 25 ml of water was also added to the cooled mixture. After standing for 15 minutes in the cold the mixture was filtered through a No. 4 glass filter. The precipitate – a bright yellow powder – was washed with 20 ml of dioxane. The filtrate was transferred into a 100 ml measuring flask.

The primary amine group content in one milliliter of this solution was determined by Van Slyke's method. This was carried out in an apparatus of Ioanisiani [10] design for the microdetermination of deamination,and the absorption of nitrogen oxides was carried out in a glass medical syringe joined with a gas microburette. The syringe was shaken for 8 minutes, and the pentamethylene was completely determined after 20 minutes.

0.306 ml N_2 (18°, 734 mm) 0.310 ml N_2 (19°, 734 mm). In 1 ml of solution, found mg N: 0.3476, 0.350, average 0.348 mg.

The precipitate from the filter (ammoniacal complex) was decomposed with alkali, with the ammonia being distilled off into titrated acid. The quantity of ammonia was found by reversible titration (4.46 ml of 0.25 N HCl) to be 0.001115 g-equiv, which corresponded to 15.6 mg N.

Thus, in the reaction mixture was found:

total content of ammonia and ammine nitrogen 0.01959 g-equiv., or 274 mg N; ammonia nitrogen 15.6 mg X 5 = 78 mg; pentamethylenediamine nitrogen 0.348 mg X 500 = 174 mg N, hence piperidine nitrogen = 22 mg .

The complete experimental data are set forth in Table 3.

The subsequent experiments were carried out by analogous methods. Only in the experiments with butyl and cyclohexyl alcohols, and also with toluene, 0.25 N H_2SO_4 was used to titrate the steam distillate, and the steam distillate was twice treated with the acid solution, after which the bases were determined by titration.

SUMMARY

1. The conditions and factors which influence the cyclization processes which are accompanied by the formation of piperidine were studied in the case of the reduction of glutaric acid dinitrile with sodium in alcohol.

2. It was found that the dinitriles of α-methyl- and α-phenylglutaric acids give in this reaction larger yields of cyclic products than the unsubstituted dinitrile.

3. A hypothesis concerning the reaction mechanism of the cyclization of dinitriles during reduction by Vyshnegradsky's method is proposed.

4. A method was worked out for determining pentamethylenediamine, piperidine, and ammonia in mixtures.

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CONVERSION OF HYDROAROMATIC ALDEHYDES AND KETONES INTO AROMATIC HYDROCARBONS BY DEHYDRATION

A. A. Petrov and N. P. Sopov

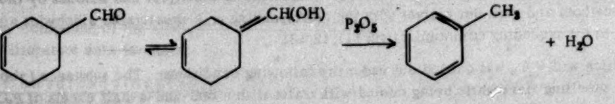
The authors of this paper have shown in their preceding works that hydroaromatic alcohols containing two double bonds in the ring and a hydroxyl group in the side chain on the carbon atom adjacent to the ring are capable of being converted into aromatic hydrocarbons [1,2], by the action of dehydrating agents. The use of dehydrating catalysts with a milder action permits one to obtain in certain cases vinylcyclohexadiene hydrocarbons as intermediate products, which correspond in structure with the initial alcohol. These hydrocarbons are readily isomerized into aromatic hydrocarbons by the action of acids. Thus, it was shown that the reaction proceeds via a stage of formation of nonbenzenic hydrocarbons, and the isomerization appears to be a process which occurs subsequent to the dehydration.

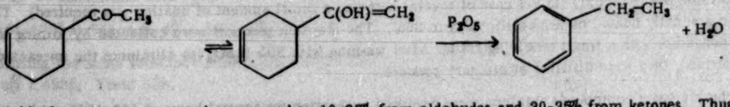
In the light of these data it is of undoubted interest to investigate in the field of dehydration of other substances with two double bonds and oxygen atoms in the side chain in the α-position to the ring. As such subjects of investigation, we chose unsaturated hydroaromatic aldehydes and ketones – products of the condensation of diene hydrocarbons and their derivatives with α, β-unsaturated aldehydes and ketones of the aliphatic series. These substances, taking into account the possibility of their existence in enolic forms, can be considered as dienic hydroaromatic alcohols, and, consequently, one can expect the formation of hydroaromatic compounds upon their dehydration.

No such isomerization has been described in the literature. However, several cases of the formation of aromatic hydrocarbons upon the heating with concentrated hydrobromic acid or zinc chloride of unsaturated hydroaromatic ketones with a double bond and a carbonyl group in the nucelus are well known [3, 4].

The compounds which we investigated did not split off water during heating with concentrated HBr. They underwent cracking on distillation with $ZnCl_2$. However, under other conditions, specifically during distillation with P_2O_5, they yielded aromatic compounds with the same number of carbon atoms. In the case of ketones, the aromatic compounds were also obtained during contact with active Al_2O_3 at 350-400°.

Thus, from Δ^3-tetrahydrobenzoic aldehyde, toluene was obtained; from Δ^3-tetrahydroacetophenone, ethylbenzene; from the homologous primary and secondary substances, the corresponding homologs of toluene and ethylbenzene, and, finally, from p-chlorotetrahydroacetophenone, p-chloroethylbenzene. The reaction can be depicted in the following manner for the two simplest cases:





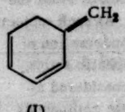
The yield of aromatic compounds amounted to 10-35% from aldehydes and 30-35% from ketones. Thus, hydroaromatic ketones yielded significantly better results. In the case of aldehydes the greater portion of the initial substance was lost as a consequence of polymerization under the influence of P_2O_5.

The condensation product of cyclopentadiene with methylvinylketone – 1-acetyl-2,5-endomethylene-cyclohexene-3 – was entirely resinified by distillation over P_2O_5, and we did not succeed in obtaining an aromatic hydrocarbon from it.

The condensation product of cyclohexadiene with methylvinyl ketone – 1-acetyl-2,5-endoethylenecyclohexene-3 – yielded a mixture of aromatic hydrocarbons in insignificant yields. By oxidizing this mixture with nitric acid, a high melting acid was obtained, the methyl ester of which melted at 129°. It is possible that this was contaminated with the dimethyl ester of terephthalic acid. This substance was not studied in greater detail.

The aromatic compounds obtained as a result of the dehydration of all the other aldehydes and ketones had constants close to those given in the literature, and during oxidation with nitric acid yielded aromatic acids, corresponding to them in structure, in a sufficiently pure state.

We can only draw certain preliminary conclusions relative to the mechanism of the described reaction. Probably the enol forms of hydroaromatic aldehydes and ketones participate in the reaction. In the case of aldehydes, the initial reaction products can only be a hydrocarbon with a semicyclic double bond (I), which, in acid medium, must rapidly rearrange into an aromatic hydrocarbon. The isomerization of the hydrocarbons of the semibenzenic series into aromatic hydrocarbons in the presence of acids proceeds readily, even if there are two alkyl groups on a given carbon atom of the ring: migration of the alkyl occurs [5,6]. In the case of hydroaromatic ketones, dehydration can lead to the formation either of an additional hydrocarbon with a semicyclic double bond (II) or (III), or the corresponding acetylenic hydrocarbon (IV). Ready conversion into aromatic hydrocarbons in the presence of dehydration catalysts is possible for all these substances. Isomerization of acetylenic hydrocarbons was not investigated directly; however, it is well known that during the dehydration, for example, of 1-acetylenylcyclohexanol-1, the formation of ethylbenzene is observed [7,8, 9]:



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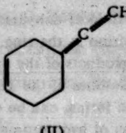

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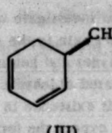

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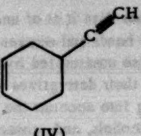

(IV)

The reaction described here of hydroaromatic aldehydes and ketones, at least in the case of ketones, is of considerable interest as a new route of conversion of diene compounds into aromatic compounds, avoiding the stage of dehydrogenation of the ring, and without there being any conversion due to the carbonyl group, which is usually employed in these cases [10].

On the other hand, this reaction permits new ways of determining the structure of homocyclization products with the participation of dienic compounds and α,β-unsaturated aldehydes and ketones, since it can be employed when other methods do not permit the reliable determination of the position of the substituent (for example, for the determination of the position of the halogen in the condensation products of β-halogenodienes with α,β-unsaturated aldehydes and ketones).

EXPERIMENTAL

The preparation of the majority of the starting hydroaromatic aldehydes and ketones by the condensation of dienic hydrocarbons and their derivatives with the corresponding α,β-unsaturated aldehydes and ketones has been described in the preceding communications [11,12,13].

The reaction with P_2O_5 was carried out under the following conditions: The substance (about 10-20 g) was stirred in a distilling flask while being cooled with water with a one-and-a-half excess of P_2O_5. The energetic reaction began quickly (in the case of several ketones, a small amount of heating was required). The mixture was then gradually heated on a metallic bath to 300°. The reaction products were collected by joining to the flask a condenser with a small receiving flask. After washing with 80% H_2SO_4 (to eliminate the unreacted starting materials), they were distilled at ordinary pressure.

The aromatic compounds obtained were oxidized by heating for several hours at 100-120° with a two-three-fold excess of 25% nitric acid in sealed glass tubes. The acids settled out on cooling the tubes, and were additionally extracted with ether and recrystallized from water. During the oxidation, the formation of small quantities of nitrocompounds was observed.

Terephthalic acid was converted, by heating with methyl alcohol and concentrated H_2SO_4 in sealed tubes for 6 hours at 100-120°, into the dimethyl ester. The latter was recrystallized from methyl alcohol.

o-Phthalic acid was converted, by heating with acetic anhydride, into the anhydride. The acetic anhydride was evaporated off in a vacuum.

The experimental data for the separate aldehydes and ketones are set forth below.

1. **Δ^3-Tetrahydrobenzoic aldehyde** (b.p. 58-59° at 18 mm, n_D^{20} 1.4738) yielded on distillation over P_2O_5 toluene with a yield of about 10%:

B.p. 109-110°, d_4^{20} 0.8623, n_D^{20} 1.4939.

Literature data [14]: b.p. 110.6°, d_4^{20} 0.8670, n_D^{20} 1.4969.

By oxidizing the substance, benzoic acid with a m.p. of 120° [15] was obtained.

2. **6-Methyl-Δ^3-tetrahydrobenzoic aldehyde** (b.p. 70-72° at 18 mm, n_D^{20} 1.4678) yielded o-xylol (12%) under the same conditions:

B.p. 142-144°, d_4^{20} 0.8808, n_D^{20} 1.5050.

Literature data [14]: b.p. 144.4°, d_4^{20} 0.8802, n_D^{20} 1.5055.

Oxidation yielded o-phthalic acid with a m.p. of 187-188°; the anhydride had a m.p. of 130.5° [15].

3. **4-Methyl-Δ^3-tetrahydrobenzoic aldehyde** (b.p. 73-75° at 18 mm, n_D^{20} 1.4732) yielded p-xylol (10%):

B.p. 136-138° at 750 mm, d_4^{20} 0.8642, n_D^{20} 1.4956.

Literature data [14]: b.p. 138.4°, d_4^{20} 0.8611, n_D^{20} 1.4958.

Terephthalic acid was obtained by oxidation of the substance The dimethyl ester melted at 140°.

4. **2,6-Dimethyl-Δ^3-tetrahydrobenzoic aldehyde** (b.p. 80-82° at 18 mm, n_D^{20} 1.4678) yielded 1,2,3-trimethylbenzene (15%):

B.p. 172-174° at 747 mm, d_4^{20} 0.8879, n_D^{20} 1.5108.

Literature data [14]: b.p. 176°, d_4^{20} 0.8944, n_D^{20} 1.5139.

Hemimellitic acid with a m.p. of 190° (from water) was obtained by oxidation. The trimethyl ester melted at 100-102°.

5. **2,4,5-Trimethyl-Δ^3-tetrahydrobenzoic aldehyde** was prepared from dimethylbutadiene and crotonaldehyde by heating for 8 hours at 120° in sealed glass tubes:

B.p. 96.5-97.5 at 18 mm, d_4^{20} 0.9274, n_D^{20} 1.4759, MR_D 46.29, calculated 45.72.

0.1400 g substance: 0.4047 g CO_2; 0.1436 g H_2O. Found %: C 78.88; H 10.27. $C_{10}H_{16}O$. Calculated %: C 78.90; H 10.6.

On distilling with P_2O_5, 2,4,5-trimethyl-Δ^3-tetrahydrobenzoic aldehyde yielded 1,2,4,5-tetramethylbenzene (durene) with a m.p. of 79° in a yield of 15%, which was in agreement with the literature data [14,15].

9.43 g substance: 29.97 mg CO_2; 9.18 mg H_2O. Found %: C 89.90; H 10.89. $C_{10}H_{14}$. Calculated %: C 89.49; H 10.56.

The molecular compound of the substance with 1,3,5-trinitrobenzene had a m.p. of 96-98°, which also corresponded to the literature data for durene [15].

6. **Δ^3-Tetrahydroacetophenone** (b.p. 77-79° at 18 mm, n_D^{20} 1.4698) yielded ethylbenzene in a yield of 35% on distillation with P_2O_5.

B.p. 134-135° at 748 mm, d_4^{20} 0.8642, n_D^{20} 1.4958.

On distilling the same substance with Al_2O_3 at 350-400°, ethylbenzene was obtained with a b.p. of 134-136°, d_4^{20} 0.8622, n_D^{20} 1.4935. Yield 35%.

Literature data [14]: b.p. 136.2°, d_4^{20} 0.8670, n_D^{20} 1.4959.

Benzoic acid with a m.p. of 119-120° (for both samples) was obtained by oxidation.

7. **2-Methyl-Δ^3-tetrahydroacetophenone** (b.p. 85-86° at 18 mm, n_D^{20} 1.4682) yielded o-methylethylbenzene with a yield of 32% on distillation with P_2O_5:

B.p. 163-165 at 752 mm, d_4^{20} 0.8807, n_D^{20} 1.5006.

Literature data [14]: b.p. 165.2°, d_4^{20} 0.8807, n_D^{20} 1.5046.

o-Phthalic acid with a m.p. of 184-185° was obtained by oxidation. The anhydride had a m.p. of 130.5°.

8. 4-Methyl-Δ^3-tetrahydroacetophenone (b.p. 91-92° at 18 mm, n_D^{20} 1.4720) yielded p-methylethylbenzene (35%) with the aid of P_2O_5:

B.p. 161-162 at 756 mm, d_4^{20} 0.8608, n_D^{20} 1.4955.

Literature data [14]: b.p. 162°, d_4^{20} 0.8612, n_D^{20} 1.4950.

Terephthalic acid was obtained by oxidation of the substance. The dimethyl ester had a m.p. of 140°.

p-Methylethylbenzene with a b.p. of 159-162°, d_4^{20} 0.8632, n_D^{20} 1.4958, was obtained by passing the substance over Al_2O_3 at 350-400°.

The results of oxidation were the same as in the preceding case.

9. 4-Chloro-Δ^3-tetrahydroacetophenone (b.p. 120-121° at 18 mm, n_D^{20} 1.4972) yielded p-chloroethylbenzene with a yield of 40%:

B.p. 178-182°, d_4^{20} 1.0290, n_D^{20} 1.5185.

0.1584 g substance: 0.1588 g AgCl. Found %: Cl 24.80. C_8H_9Cl. Calculated %: Cl 25.22.

The literature data for p-chloroethylbenzene: b.p. 179-180°, d_4^{20} 1.0575, n_D^{20} 1.5223.

Thus, the substance obtained by us was not entirely pure. However, upon oxidation it yielded the expected p-chlorobenzoic acid with a m.p. of 240°.

10. 1-Acetyl-2,5-endomethylenecyclohexene-3 was prepared by the condensation of cyclopentadiene with methylvinylketone. The reaction proceeded even at room temperature. The condensation product had:

B.p. 84-86° at 18 mm, d_4^{20} 1.0090, n_D^{20} 1.4856, MR_D 38.72, $C_9H_{12}O$, calculated 38.90.

No distillate was obtained upon distillation with P_2O_5. Complete resinification occurred.

11. 1-Acetyl-2,5-endoethylenecyclohexene-3 (b.p. 106-107° at 18 mm, n_D^{20} 1.4951) yielded during distillation over P_2O_5 a very small quantity of an oil which distilled in the range 150-200°, d_4^{20} 0.9270, n_D^{20} 1.5096.

A small quantity of high melting acid, the methyl ester of which melted at 129°, was obtained by the oxidation of this distillate.

SUMMARY

1. It was shown that upon distillation with P_2O_5 or with Al_2O_3 at 350-400°, unsaturated hydroaromatic ketones, and in the case of P_2O_5, aldehydes also, formed during the condensation of diene hydrocarbons and their derivatives with α,β-unsaturated aldehydes and ketones of the fatty series, undergo dehydration with the formation of aromatic compounds.

2. It was suggested that this reaction be used for the determination of the structure of products of the diene synthesis.

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THERMOCATALYTIC CONVERSIONS OF BUTYLNAPHTHALENES

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In recent years a number of works on the thermal and thermocatalytic conversion of alkylbenzenes has been published. At a temperature of 450° and higher, the decomposition of the alkylbenzene molecule into an olefin and benzene occurs [1,2,3,4]:

$$C_6H_5C_nH_{2n+1} \longrightarrow C_6H_6 + C_nH_{2n}$$

The works of Dobryansky and his coworkers showed that the simplest alkylbenzenes at temperatures of 150-300° and in the presence of activated natural aluminum silicates transfer unchanged fatty radicals according to the scheme

$$2C_6H_5R \rightleftharpoons C_6H_6 + C_6H_4R_2$$

$$2C_6H_4R_2 \rightleftharpoons C_6H_5R + C_6H_3R_3$$

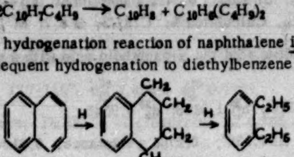
Thus, xylene, ethylbenzene, isopropylbenzene, secondary butylbenzene undergo this conversion to respective extents of 40, 62, 73 and 64% [5,6].

It is of very great interest to study the indicated reaction in representatives of the alkylated condensed aromatic hydrocarbons — the alkylnaphthalenes. In the literature there are only data on the pyrolysis of butylnaphthalene at 650° with the formation of hydrocarbon gases, naphthalene and dinaphthyl [7].

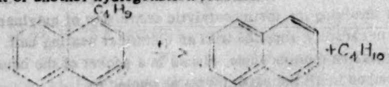
We investigated the thermocatalytic conversion of mono- and di-sec.-butylnaphthalenes over activated natural aluminum silicate catalyst. The experiments with sec.-butylnaphthalene showed that during heating in an autoclave at 300° for 6 hours the starting material underwent approximately 80% conversion. The chief reaction under these conditions was the conversion of the α-isomer into the thermally more stable β-isomer. A parallel reaction consisted in the formation of dibutylnaphthalene and naphthalene due to the conversion of the butyl radical

$$2C_{10}H_7C_4H_9 \longrightarrow C_{10}H_8 + C_{10}H_6(C_4H_9)_2$$

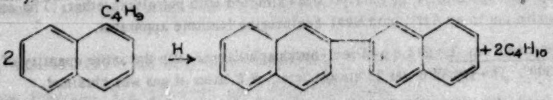
There also took place a hydrogenation reaction of naphthalene in statu nascendi, with the formation of tetrahydronaphthalene with subsequent hydrogenation to diethylbenzene with rupture of the polymethylene ring



Butane is formed as the result of another hydrogenation reaction



The formation of dinaphthyl can be explained as due to these same causes



The formation of dinaphthyl from naphthalene with the evolution of hydrogen, in view of the greater thermal stability of naphthalene and the comparatively low temperature of our experiments, should be considered as hardly probable.

In the experiment with disecondary butylnaphthalene at a temperature of 280°, the total conversion of the initial hydrocarbon reached approximately 85%. We isolated, in addition to butane, 3,4-dimethylhexane, which arose, evidently, due to the combination of two butyl radicals:

$$2C_{10}H_6(C_4H_9)_2 \xrightarrow{H} 2C_{10}H_7C_4H_9 + C_8H_{18}$$

The thus formed mono-secondary-butylnaphthalene in the process of thermocatalytic conversion yielded the same products that were evolved in the first experiment.

As a result of the hydrogenation reactions indicated above, carboids (coke-like substances on the catalyst) were formed, impoverished in hydrogen, and substances contained in the residue during distillation and consisting of a mixture of highly condensed aromatic hydrocarbons. These residues contained 94.93% C and 4.63% H at the same time that the initial monobutylnaphthalene contained 91.16% C and 8.74% H. The possibility of the additional participation in these reactions of the hydrogen, which enters into the composition of the activated aluminum silicates is not excluded.

The results observed by us rather graphically illustrate the process of conversion of petroleum in nature under the influence of heat and the catalytic influence of the clays which accompany the rock. This process proceeds, as is well-known, from the high-molecular-weight and highly cyclized substances, primarily of aromatic structure, via naphthenic hydrocarbons, to methane hydrocarbons as the final conversion products [8].

In our experiments the processes of simplification of the molecules of the initial alkylnaphthalenes are fundamental; in particular, the hydrogenation processes proceed due to the redistribution of hydrogen with the formation of mixed naphthenic-aromatic hydrocarbons (tetrahydronaphthalene), alkylbenzenes (diethylbenzene) and methane hydrocarbons (butane and octane).

In comparing the conversions which were studied of alkylnaphthalenes and alkylbenzenes, the greater reactive capacity of alkylnaphthalenes and lesser strength of the naphthalenic nucleus in comparison with alkylbenzenes should be noted.

EXPERIMENTAL

Activated gumbrin – natural clay of the montmorillonite type – was used as the catalyst. The activation was carried out with 15% hydrochloric acid during heating on a water bath for 12 hours with continuous stirring. After washing off the hydrochloric acid, the catalyst was shaped and dried at 300°.

The mono- and dibutylnaphthalenes were prepared by Tsukervanik's method [9], from naphthalene and n-butyl alcohol in the presence of aluminum chloride. The yields of alkylnaphthalenes did not exceed 35%.

α-Sec.-butylnaphthalene. B.p. 272-274°; n_D^{20} 1.5701; d_4^{20} 0.9742.

0.7308 g substance; 8.05 g benzene: Δt 2.55°. 0.3412 g substance: 1.1410 g CO_2; 0.2667 g H_2O. Found %: C 91.16; H 8.74; M 182.3. $C_{14}H_{16}$. Calculated %: C 91.3; H 8.7; M 184.0

By oxidation during boiling with 5% nitric acid the α-naphthoic acid with a m.p. of 161° was obtained. The picrate melted at 77°.

Di-Sec.-butylnaphthalene. b.p. 310-320°; n_D^{20} 1.5626; d_4^{20} 0.9545.

0.3293 g substance; 8.46 g benzene: Δt 0.839°. 0.2766 g substance: 0.9104 g CO_2; 0.2426 g H_2O. Found %: C 89.76; H 9.81; M 237.9. $C_{18}H_{24}$. Calculated %: C 90.0; H 10.0; M 240.0.

All the experiments involving the thermocatalytic conversion of butylnaphthalenes were carried out in a steel autoclave, 0.8 liter in capacity, supplied with an electrical heating unit. The temperature was measured with the use of a copper constantan thermocouple, placed in a pocket of the housing of the autoclave. The weight ratio of catalyst and hydrocarbon in all the experiments amounted to 1: 1.

After the experiments the catalyst was extracted with petroleum ether. The analysis of the gaseous products was carried out in an All-Union Heat-Engineering Institute apparatus.

Experiment No. 1. 214.8 g of sec.-butylnaphthalene with the same quantity of catalyst was heated for 6 hours at 300°. The pressure was 23 atmospheres. 2.6 liters of gas was obtained.

Analysis of the gas in %: CO_2 1.0; O_2 1.2; CO 0.2; H_2 6.45; C_4H_{10} 83.95; N_2 (by difference) 7.2. The following basic fractions were isolated by fractional distillation of the liquid products:

Diethylbenzene Fraction. B.p. 177-183°; n_D^{20} 1.4969; d_4^{20} 0.8621.
0.3585 g substance; 16.28 g benzene: Δt 0.880°. 0.1914 g substance; 16.45 g benzene: Δt 0.465°. Found: M 128.4, 128.5. $C_{10}H_{14}$. Calculated: M 134.

By oxidation of the fraction with an aqueous solution of potassium permanganate, phthalic acid was obtained in which the quantity of acid groups was determined.

0.0735 g of acid: 12.41 ml of 0.1 N alkali, 3.70 ml of 0.1 N H_2SO_4 consumed in back titration. Found %: COOH 53.6. $C_6H_4(COOH)_2$. Calculated %: COOH 54.2.

Tetrahydronaphthalene Fraction. B.p. 206-208°; n_D^{20} 1.5410; d_4^{20} 0.9694.

0.1263 g substance; 11.3 g benzene: Δt 0.432°. 0.2136 g substance: 0.7112 g CO_2; 0.1728 g H_2O. Found %: C 90.87; H 9.00; M 130. $C_{10}H_{12}$. Calculated %: C 90.91; H 9.09; M 132.

Naphthalene Fraction. B.p. 217-220° The recrystallized substance melted at 80°.

α-Sec.-butylnaphthalene Fraction. B.p. 272-276°; n_D^{20} 1.5706; d_4^{20} 0.9730.

0.2102 g substance; 12.71 g benzene: Δt 0.462°. 0.4374 g substance; 12.74 g benzene: Δt 0.960°. 0.2316 g substance; 0.7728 g CO_2; 0.1794 g H_2O. Found %: C 91.05; H 8.67; M 184.0, 182.5. $C_{14}H_{16}$. Calculated %: C 91.3; H 8.7; M 184.

M.p. of α-naphthoic acid 161°.

β-Sec.-butylnaphthalene Fraction. B.p. 285-287°; n_D^{20} 1.5798; d_4^{20} 0.9742.

0.2248 g substance; 19.0 g benzene: Δt 0.327°. 0.4386 g substance; 19.0 g benzene: Δt 0.639°. 0.1816 g substance: 0.6052 g CO_2; 0.1454 g H_2O. Found %: C 90.89; H 8.95; M 185.7, 185.3. $C_{14}H_{16}$. Calculated %: C 91.3; H 8.7; M 184.0.

M.p. of β-naphthoic acid 181°.

Dibutylnaphthalene Fraction. B.p. 138-140° (2 mm); n_D^{20} 1.5614; d_4^{20} 0.9540.

1.0846 g substance; 16.85 g benzene: Δt 0.240°. 0.1710 g substance; 15.93 g benzene: Δt 0.235°. 0.1390 g substance: 0.4568 g CO_2; 0.1246 g H_2O. Found %: C 89.67; H 10.02; M 234.3, 238.0. $C_{18}H_{24}$. Calculated %: C 90.0; H 10.0; M 240.

Dinaphthyl Fraction. B.p. 227-229° (2 mm). M.p. 186.5°.

0.0652 g substance: 13.56 g benzene; Δt 0.098°. 0.0794 g substance; 13.56 g benzene: Δt 0.120°. Found: M 251.7, 250.3. $C_{20}H_{14}$. Calculated: M 254.

The values for the yields obtained by fractional distillation of the substances are set forth in Table 1.

Experiment No. 2. 184 g of di-sec.-butylnaphthalene was heated for 16 hours at 275°. The maximum pressure was 31 atm. 3.5 liters of gas was obtained The analysis of the gas in %: CO_2 0.5; O_2 2.05; CO 1.15; H_2 12.6; C_4H_{10} 70.1; N_2 12.6.

The following fractions were obtained by fractional distillation of the liquid products.

Octane Fraction. B.p. 117-119°; n_D^{20} 1.4048; d_4^{20} 0.7199.

0.1962, 0.3477 g substance; 15.52, 15.52 g benzene: Δt 0.595, 1.050°. Found: M 108.9, 109.4. C_8H_{18}. Calculated: M 114.

Diethylbenzene Fraction. B.p. 177-183°; n_D^{20} 1.4966; d_4^{20} 0.8622.

0.2042, 0.1964 g substance; 13.68, 12.76 g benzene: Δt 0.583, 0.594°. Found: M 131.2, 132.8. $C_{10}H_{14}$. Calculated: M 134.

Tetrahydronaphthalene Fraction, B.p. 206-208°; n_D^{20} 1.5412; d_4^{20} 0.9690.

0.2462, 0.1978 g substance; 14.33, 13.47 g benzene: Δt 0.685, 0.574°. Found: M 128.7, 131.1. $C_{10}H_{12}$. Calculated: M 132.

Naphthalene Fraction. B.p. 217-220° The recrystallized substance melted at 80.2°.

α-Sec.-butylnaphthalene Fraction: B.p. 272-276°; n_D^{20} 1.5710; d_4^{20} 0.9730.

0.2688, 0.4692 g substance; 12.99, 12.99 g benzene: Δt 0.605, 1.008°. Found: M 183.7, 184. $C_{14}H_{16}$. Calculated: M 184.

β-Sec.-butylnaphthalene Fraction. B.p. 285-287°; n_D^{20} 1.5792; d_4^{20} 0.9748.

0.1674, 0.1578 g substance; 13.14, 12.62 g benzene: Δt 0.348, 0.340°. Found: M 187.8, 188.7. $C_{14}H_{16}$. Calculated: M 184.

TABLE 1

Substance	Yield	
	In g	In % of the butylnaphthalene taken
Diethylbenzene	5.8	2.7
Tetrahydronaphthalene	4.9	2.2
Naphthalene	47.1	22.1
α-Sec.-butylnaphthalene	42.2	19.7
β-Sec.-butylnaphthalene	37.7	17.2
Dibutylnaphthalene	9.2	4.3
Dinaphthyl	8.5	3.9
Coke on the catalyst	14.2	6.6
Residue	27.4	12.9
Loss	15.5	7.3
Total:	212.5	98.9

TABLE 2

Fraction	Yield	
	In g	In % of the dibutylnaphthalene taken
Octane	17.5	9.5
Diethylbenzene	7.1	4.4
Tetrahydronaphthalene	11.2	6.1
Naphthalene	26.1	14.2
α-Sec.-butylnaphthalene	19.6	10.7
β-Sec.-butylnaphthalene	15.0	8.2
Dibutylnaphthalene	28.5	15.5
Dinaphthyl	7.9	4.3
Coke on the catalyst	21.5	11.7
Residue after fractional distillation	13.8	7.2
Loss	13.0	6.8
Total:	181.4	98.6

Dibutylnaphthalene Fraction. B.p. 138-140° (2 mm); n_D^{20} 1.5610; d_4^{20} 0.9544.

0.2064, 0.5140 g substance; 12.06, 12.06 g benzene: Δt 0.370, 0.900°. Found: M 237.3, 243.0. $C_{18}H_{24}$. Calculated: M 240.

Dinaphthylene Fraction. B.p. 227-229° (2 mm). M.p. 186.2°.

0.1912, 0.2142 g substance; 14.10, 13.75 g benzene: Δt 0.278, 0.322°. Found: M 250, 247.6. $C_{20}H_{14}$. Calculated: M 254.

The values of the yields obtained by fractional distillation of the substances are set forth in Table 2.

SUMMARY

1. The thermocatalytic conversions of mono- and di-sec.-butylnaphthalenes over natural aluminum silicate catalyst were studied.

In addition to the typical alkylbenzene reactions involving the migration of unchanged fatty radicals, a number of other reactions were observed. The most characteristic of them were the formation of diethylbenzene, tetrahydronaphthalene, dinaphthyl and butane, proceeding via the redistribution of hydrogen and also the formation of octane (3,4-dimethylhexane), evidently due to the combination of butyl radicals.

The results obtained confirm the general rule which specifies the following direction for the conversion processes of petroleum in nature: aromatic hydrocarbons ⟶ naphthenic hydrocarbons ⟶ methane hydrocarbons.

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ACTION OF ALKYL HALIDES AND ALLYL BROMIDE ON SODIUM DIBUTYLTHIOPHOSPHITE

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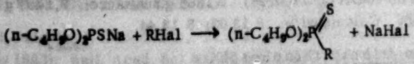
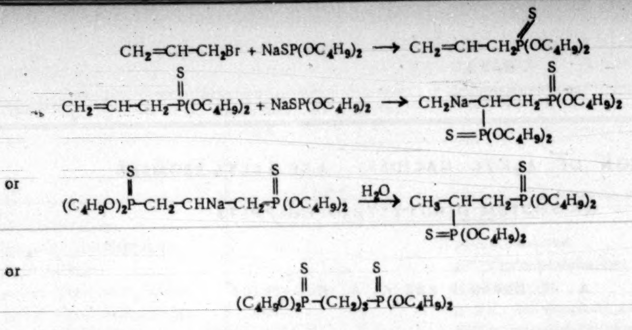
The action of alkyl halides on salts of dialkylphosphorous acids has been studied in sufficient detail at the present time, and is one of the most important methods of synthesizing the esters of alkylphosphinic acids. The reactions between the salts of dialkylphosphorous acids and allyl halide compounds was studied by one of us only in the last few years, and led to very interesting and important conclusions. It was shown that, depending on the presence or absence in the reaction mixture of excess dialkylphosphorous acid or of solvent, the reaction leads to different results [1]. In the first case, allylphosphinic esters are formed in quantitative yield; in the second case, in addition to the allylphosphinic esters, the products of addition to them of dialkylphosphorous acid molecules were isolated primarily, and in certain cases exclusively. The possibility of direct addition of dialkylphosphorous acids at the double bond of allylphosphinic esters was confirmed in special experiments. The results obtained were the basis for working out a new method of synthesizing the esters of phosphinic and thiophosphinic acids, consisting in the addition of various reagents to unsaturated compounds of the electrophile type [2]. In the development and extension of works previously carried out, we studied the reaction between dialkylthiophosphites, alkyl halides and allyl halide compounds. This investigation, as it appeared to us, could be of interest both from the point of view of the study of the mechanism of the indicated reactions, and for working out a method of synthesizing esters of alkylthiophosphinic acids. The esters of alkylthiophosphinic acids have hardly been studied at all until very recently. It was only in 1952 that Arbuzov and Rizpolozhensky [3] and Razumov and Mukhacheva and Sim-Do-Khen [4] proposed an accessible method for preparing them, consisting of the addition of sulfur to esters of alkylphosphinous acids. In a second variant of this method, the preparation of esters of alkylthiophosphinic acids was proposed via the addition of sulfur to alkyldichlorophosphine with subsequent treatment of the product formed with sodium alcoholate As a result of the working out of a method of synthesis of dialkylthiophosphorous acids, the possibility of synthesizing esters of alkylthiophosphinic acids with the aid of alkaline metal salts of dialkylthiophosphorous acids became evident. Kabachnik and Mastryukova carried out a reaction between diethylsodium diethylthiophosphite, ethyl iodide, benzyl chloride and chloroacetic ester [5]. We also, before entering upon the study of the reactions between dialkylthiophosphites and halogen allyl compounds, carried out a number of reactions with alkyl halides In contrast to the diethylthiophosphites, the alkaline metal salts of diethylthiophosphorous acid were poorly soluble in ether and benzene. The experiments carried out by us with ethyl iodide and the sodium and lithium salts of diethylthiophosphorous acid led to the formation of the ethyl ester of ethylthiophosphinic acid. However, the yields of it were insufficiently high; therefore in further experiments we substituted sodium diethylthiophosphite for sodium dibutylthiophosphite. The latter was considerably more soluble in ether and benzene,and the reaction with them proceeded almost as readily as with sodium diethylphosphite. The precipitate of sodium bromide formed in the reaction process was filtered off or eliminated by treatment of the reaction mixture with water. Experiments were carried out with ethyl iodide, propyl iodide, butyl bromide, and chloromethylbutyl ether. In all cases the butyl esters of the corresponding alkylthiophosphinic acids were isolated in yields of 60-70%.



$$(n\text{-}C_4H_9O)_2PSNa + RHal \longrightarrow (n\text{-}C_4H_9O)_2P(=S)R + NaHal$$

As a result of the reaction between sodium dibutylthiophosphite and allyl bromide two products were obtained: a low boiling product (b.p. 120° at 3 mm) which appeared to be the butyl ester of allylthiophosphinic acid,and a high boiling product (b.p. 207° at 3 mm), corresponding, according to the analytical data for sulfur and phosphorus, to di(dibutylthiophosphono)propane. The course of the reaction can be represented by the following scheme:



$$CH_2{=}CH{-}CH_2Br + NaSP(OC_4H_9)_2 \longrightarrow CH_2{=}CH{-}CH_2\overset{S}{\overset{\|}{P}}(OC_4H_9)_2$$

$$CH_2{=}CH{-}CH_2{-}\overset{S}{\overset{\|}{P}}(OC_4H_9)_2 + NaSP(OC_4H_9)_2 \longrightarrow CH_2Na{-}\underset{S{=}P(OC_4H_9)_2}{\underset{|}{CH}}{-}CH_2{-}\overset{S}{\overset{\|}{P}}(OC_4H_9)_2$$

or

$$(C_4H_9O)_2\overset{S}{\overset{\|}{P}}{-}CH_2{-}CHNa{-}CH_2{-}\overset{S}{\overset{\|}{P}}(OC_4H_9)_2 \xrightarrow{H_2O} CH_3{-}\underset{S{=}P(OC_4H_9)_2}{\underset{|}{CH}}{-}CH_2{-}\overset{S}{\overset{\|}{P}}(OC_4H_9)_2$$

or

$$(C_4H_9O)_2\overset{S}{\overset{\|}{P}}{-}(CH_2)_3{-}\overset{S}{\overset{\|}{P}}(OC_4H_9)_2$$

The structure of di(dibutylthiophosphono)propane, as regards the choice of one of the two possible isomeric forms, remains as yet unestablished. Thus, the reaction of sodium dibutylthiophosphite with allyl bromide, by analogy with the reactions of dialkylphosphites, also proceeds in two phases: initially a substitution reaction proceeds, and then, depending on the ratio of reagents and the conditions under which the experiment is carried out, the addition reaction of dibutylthiophosphorous acid at the double bond of allylthiophosphinic ester proceeds.

EXPERIMENTAL

Action of Ethyl Iodide on Sodium Diethylthiophosphite

13 g of diethylthiophosphorous acid was slowly introduced in drops into 2 g of metallic sodium, pressed in the form of wires, in 200 ml of dry toluene. The reaction was initially carried out in the cold, and then during heating on a water bath and with continuous stirring until the evolution of hydrogen ceased. The sodium derivative was evolved in the reaction process in the form of a voluminous, finely crystalline, white precipitate. 20 g of ethyl iodide was slowly added to the thus-obtained sodium derivative during uninterrupted stirring. The reaction mixture was heated on a water bath for 3 hours. The sodium iodide was filtered off, the toluene distilled off at 90 mm; the residue, which consisted of a thick, oily liquid of an unpleasant odor, was vacuum distilled from an Arbuzov flask. As a result of two distillations, 6.8 g of diethyl ester of ethylthiophosphinic acid with a b.p. of 79-80° at 12 mm; n_D^{20} 1.4555; d_4^{20} 1.0338, was obtained.

0.1542, 0.1506 g substance: 40.9, 40.5 ml NaOH (T = 0.0226). 0.1569, 0.1642 g substance: 0.2027, 0.2109 g $BaSO_4$. Found %: P 16.60, 16.83; S 17.82, 17.61. $C_6H_{15}O_2PS$. Calculated %: P 17.03; S 17.57.

The product obtained by us was identical according to its properties with that obtained by Kabachnik and Mastryukova [5].

Action of Ethyl Iodide on Sodium Dibutylthiophosphite

Sodium dibutylthiophosphite was prepared from 14 g of dibutylthiophosphorous acid, 2 g of sodium and 250 ml of absolute ether. The unreacted sodium was removed mechanically from the solution with the aid of long glass needles. 14.8 g of ethyl iodide was then slowly introduced in drops into the sodium dibutylthiophosphite solution during stirring with a mechanical stirrer. The reaction mixture was heated on a water bath for 3 hours. After cooling in a flask, a small (but sufficient for dissolving the sodium iodide precipitate which had formed) quantity of water was added, after which the entire reaction mixture was transferred to a separatory funnel. The ethereal layer was separated off and dried with calcium chloride. After distilling off the ether, the residue was vacuum distilled. 9.6 g of the dibutyl ester of ethylthiophosphinic acid with a b.p. of 97-98° at 2 mm; n_D^{20} 1.4510; d_4^{20} 0.9768, was obtained

0.1156, 0.1252 g substance: 23.4, 25.6 ml NaOH (T = 0.0226). 0.1666 g substance: 0.1497 g $BaSO_4$. Found %: P 12.68, 13.09; S 13.13. $C_{10}H_{23}O_2PS$. Calculated %: P 13.03; S 13.44.

Action of Propyl Iodide on Sodium Dibutylthiophosphite

10 g of propyl iodide was slowly introduced in drops into a stirred ethereal solution of sodium dibutylthiophosphite, prepared from 9.8 g of dibutylthiophosphorous acid, 1.3 g of sodium and 250 ml of absolute ether. After the reaction mixture had been heated for three hours on a water bath, it was cooled and treated with water. After separation and drying of the ethereal layer, the ether was distilled off, and the residue vacuum distilled. 5.9 g of the dibutyl ester of propylthiophosphinic acid with a b.p. of 103-104° at 2 mm; n_D^{20} 1.4580; d_4^{20} 0.9772, was obtained.

0.1340 g substance: 70.7 ml NaOH (T = 0.00880). 0.1304, 0.1544 g substance: 0.1217, 0.1464 g $BaSO_4$. Found %: P 12.86; S 12.82, 13.01. $C_{11}H_{25}O_2PS$. Calculated %: P 12.56; S 12.70.

Action of Butyl Bromide on Sodium Dibutylthiophosphite

11 g of butyl bromide was introduced in drops into an ethereal solution of sodium dibutylthiophosphite, prepared from 10 g of dibutylthiophosphorous acid, 1.3 g of sodium and 250 ml of ether. The subsequent reaction and treatment of the reaction mixture were carried out analogously to those described in the preceding experiments. As a result 6.7 g of the dibutyl ester of butylthiophosphinic acid with a b.p. of 108-109° at 2 mm; n_D^{20} 1.4654; d_4^{20} 0.9780 was obtained.

0.1410 g substance: 25.1 ml NaOH (T = 0.0226). 0.1115, 0.1205 g substance: 0.1012, 0.1032 g $BaSO_4$. Found %: P 11.14; S 12.46, 12.32. $C_{12}H_{27}O_2PS$. Calculated %: P 11.65; S 12.03.

Action of Chloromethylbutyl Ether on Sodium Dibutylthiophosphite

The ethereal solution of sodium dibutylthiophosphite was prepared from 9.9 g of dibutylthiophosphorous acid, 1.5 g of sodium and 250 ml of ether. The excess sodium was eliminated from the solution mechanically with the aid of a glass needle. The reaction was carried out with 10 g of chloromethylbutyl ether. After completion of the reaction, the reaction mixture was treated with water, the ethereal solution was dried with sodium sulfate, the ether was distilled off on a water bath, the residue vacuum distilled. 8.6 g of the dibutyl ester of butoxymethylthiophosphinic acid with a b.p. of 146-148° at 5 mm; n_D^{20} 1.4482; d_4^{20} 0.9806, was obtained.

0.1340, 0.1412 g substance: 21.63, 22.66 ml NaOH (T = 0.0226). 0.1456, 0.1170 g substance: 0.1185, 0.0963 g $BaSO_4$. Found %: P 10.10, 10.04; S 11.18, 10.30. $C_{23}H_{29}O_3PS$. Calculated %: P 10.47, S 10.81.

Action of Sodium Dibutylthiophosphite on Allyl Bromide

18.5 g of allyl bromide was introduced in drops into a stirred ethereal solution of sodium dibutylthiophosphite, prepared from 20 g of dibutylthiophosphorous acid, 2 g of sodium and 300 ml of absolute ether. The reaction mixture was heated on a water bath for 2 hours, treated with water, the ethereal layer was dried with sodium sulfate, the ether driven off, and the residue vacuum distilled. The following were obtained: a) 10.1 g of the dibutyl ester of allylthiophosphinic acid with a b.p. of 120° at 3 mm; n_D^{20} 1.4710; d_4^{20} 0.9858.

0.1248, 0.1418 g substance: 23.94, 26.95 ml NaOH (T = 0.0226). 0.1402, 0.1436 g substance: 0.1348, 0.1352 g $BaSO_4$. Found %: P 12.00, 11.89; S 13.20, 12.96. $C_{11}H_{23}O_2PS$. Calculated %: P 12.40; S 12.80.

b) 2.6 g of di(dibutylthiophosphono)propane in the form of colorless, viscous liquid with a b.p. of 207° at 3 mm; n_D^{20} 1.4643.

0.1312, 0.1278 g substance; 27.81, 27.80 ml NaOH (T = 0.0226). 0.1314, 0.1196 g substance: 0.1361, 0.1261 g $BaSO_4$. Found %: P 13.26, 13.61; S 14.22, 14.48. $C_{19}H_{42}O_4P_2S_2$. Calculated %: P 13.33; S 13.92.

SUMMARY

1. The action of alkyl halides on sodium dibutylthiophosphite was studied. The dibutyl esters of the following were synthesized: ethyl-, n-propyl-, n-butyl-, and butoxymethylthiophosphinic acids.

2. It was shown that during the action of sodium dibutylthiophosphite on allyl bromide, along with the substitution reaction, an addition reaction of dibutylthiophosphorous acid at the double bond of the allylthiophosphinic ester also proceeds.

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* See Consultants Bureau Translation, page 2107.

** See Consultants Bureau Translation, 423.

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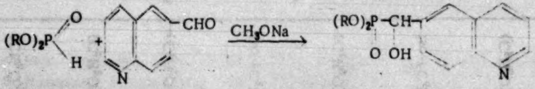
REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

VII. ESTERS OF α-HYDROXY(6-QUINOLYL)METHYLPHOSPHINIC ACID

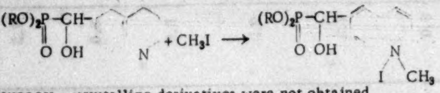
V. S. Abramov and A. S. Kapustina

The reaction of dialkylphosphorous acids with carbonyl compounds [1] was successfully extended by us to aldehydes of the heterocyclic series. 6-Quinoline aldehyde reacts with various dialkylphosphorous acids and forms the corresponding esters of α-hydroxy(6-quinolyl)-methylphosphinic acid, according to the scheme



We carried out the reaction of 6-quinoline aldehyde with dimethyl-, diethyl-, dipropyl-, diisopropyl-, dibutyl-, diisobutyl-, and diallylphosphorous acids; consequently, R in the scheme will respectively be CH_3, C_2H_5, C_3H_7, C_3H_7-iso, C_4H_9, C_4H_9-iso, and C_3H_5. The reaction proceeds rapidly with the evolution of heat. Colorless viscous syrups are formed. 6-Quinoline aldehyde was selected by us as the carbonyl compound because we expected to obtain the esters of α-hydroxy-(6-quinolyl)methylphosphinic acid in the crystalline form. This was important for readily obtaining them in the pure form, since the application of fractional distillation for the purification of such comparatively high molecular weight compounds could not give positive results. We had previously shown that the esters of α-hydroxyalkylphosphinic acids are decomposed during distillation (heating) into the initial substances, and the more readily for a given dialkylphosphorous acid, the higher the total molecular weight of the ester, and the higher the weight of the radical bound to the phosphorus atom [2].

Our expectations of obtaining crystalline products were not correct. Only one isopropyl ester of α-hydroxy-(6-quinolyl)methylphosphinic acid with a m.p. of 119-120° was obtained in the crystalline form. We had, moreover, planned in the case of formation of noncrystalline syrups, their conversion into ammonium derivatives or the preparation of their picrates. The latter we proposed to isolate in the crystalline state. The few experiments carried out by us involving the action of alkyl halides on the esters of α-hydroxy(6-quinolyl)methylphosphinic acids with the object of preparing halogen substituted ammonia



were not crowned with success — crystalline derivatives were not obtained.

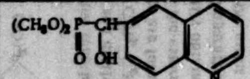
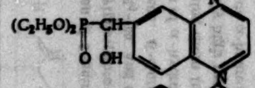
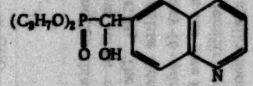
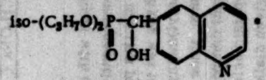
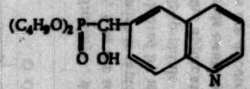
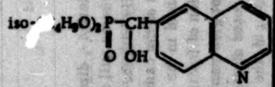
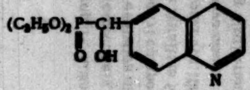
By the reaction of the esters of α-hydroxy(6-quinolyl)methylphosphinic acid with picric acid, excellently crystallizing picrates were formed. The picrates were obtained either directly or by pouring the esters of α-hydroxy(6-quinolyl)methylphosphinic acid with a saturated solution of picric acid in alcohol or after boiling the solution for a brief time. The picrates consisted of well-formed, needle-like crystals with an orange color. The picrates were recrystallized from ethyl alcohol; methyl and butyl alcohols were also employed.

The results of the reactions investigated, involving the reaction of 6-quinoline aldehyde with various dialkylphosphorous acids, and also the characteristics of the picrates obtained, and of the esters of α-hydroxy-(6-quinolyl)methylphosphinic acid formed, are set forth in the table.

EXPERIMENTAL

Reaction of Dialkylphosphorous Acids with 6-Quinoline Aldehyde

An equimolecular mixture of the dialkylphosphorous acid and 6-quinoline aldehyde was prepared, which was then carefully heated to complete solution of the 6-quinoline aldehyde in the acid. The solution was cooled to room temperature or to a temperature at which crystallization began. The temperature of the solution

Dialkylphosphorous acid	Quantity of reacting substances (in g)		Increase in temperature (in °)	Esters obtained	Yield of ester (in %)	M.p. of the picrate (in °)	Yield of picrate (in g)	Content of phosphorus in the picrate (in %)	
	Acid	6-Quinoline aldehyde						Calculated	Found
$(CH_3O)_2POH$	2.2	3.0	40-67		75.0	170-171	7.3	6.02	5.58, 5.86
$(C_2H_5O)_2POH$	1.8	2.0	19-96		44.5	152	3.0	5.87	5.51, 5.32
$(C_3H_7O)_2POH$	3.4	3.2	42-105		53.2	151-152	6.0	5.57	5.43, 5.52
iso-$(C_3H_7O)_2POH$	1.7	1.6	36-62	 *	39.0	146-147	2.2	5.57	5.68, 5.65
$(C_4H_9O)_2POH$	3.9	3.14	45-65		62.7	157-158	7.3	5.30	5.21, 5.35
iso-$(C_4H_9O)_2POH$	3.9	3.14	23-67		51.5	150-150.5	6.0	5.30	5.24, 5.35
$(C_3H_5O)_2POH$	3.9	3.14	35-83		84.5	167	9.2	5.61	5.40

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* The crystalline substance has a m.p. of 119-120°. Found %: P 9.44, 9.25. $C_{16}H_{22}O_4NP$. Calculated %: P 9.65.

was measured and a freshly prepared saturated solution of sodium methylate was added in drops. After the addition, an increase in temperature was observed. The product which formed ordinarily consisted of a transparent, viscous syrup. The product was cooled to a low temperature (with a mixture of snow and salt), but only the isopropyl ester of α-hydroxy(6-quinolyl)methylphosphinic acid was obtained in the crystalline state. After recrystallization from cyclohexane, its melting point was 119-120°.

The noncrystallized syrups were mixed with an equimolecular quantity of picric acid dissolved in alcohol. A precipitate of the picrate ordinarily settled out at once. Only in isolated cases was an insignificant amount of heating carried out. The picrate was recyrstallized from methyl, ethyl or butyl alcohol. The melting points of the picrates are set forth in the table. The phosphorus content of the picrates was determined. The analysis and yields of the esters are also set forth in the table.

SUMMARY

The action of dialkylphosphorous acids on 6-quinoline aldehyde was studied. Seven new esters of α-hydroxy-(6-quinolyl)methylphosphinic acid were obtained and isolated from the reaction products in the form of the picrates. The isopropyl ester of α-hydroxy(6-quinolyl)methylphosphinic acid was prepared in the form of colorless, regular crystals with a m.p. of 119-120°.

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* See Consultants Bureau Translation, page 709.

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INVESTIGATIONS IN THE FIELD OF QUINOLINE DERIVATIVES

XI. SYNTHESIS OF LEPIDINE AND ITS DERIVATIVES FROM ACETYLATED ARYLAMINES

B. I. Ardashev and B. A. Tertov

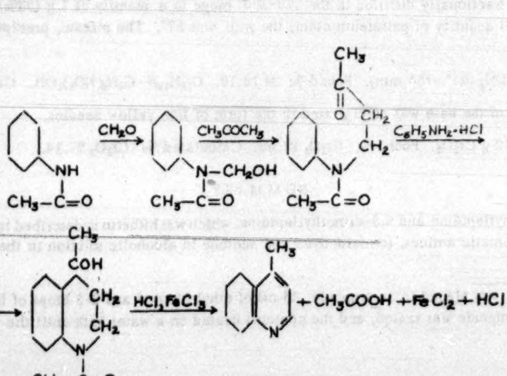
We previously noted that α-substituted quinolines are considerably more accessible than γ-substituted quinolines [1]. The Knorr method is ordinarily employed for the synthesis of lepidine and its derivatives and gives excellent yields. The conversion from hydroxy derivative to lepidine was successfully solved in 1936 by G. I. Mikhailov by the action of phosphorus oxychloride, with subsequent reduction of the chloro derivative by tin and hydrochloric acid [2, 3].

However, even though there have been substantial refinements in the Knorr reaction, it retains its basic defect – the fact that it proceeds in several stages and is rather unwieldy and prolonged. Other methods are also practically difficult on account of the insufficient accessibility of the starting materials, or unsuitable as a consequence of the low yields of lepidine, the long time required for accomplishing the reaction, and for a number of other reasons [3].

Beyer's method, by which lepidine and its derivatives can be obtained from primary aromatic amines, formaldehyde and acetone [4], i.e., from readily accessible starting materials, gives low yields of lepidine and its substituted derivatives, which do not exceed 4-5% of the theoretical [5]. As a result, a sufficiently convenient preparative method for the synthesis of lepidine and its derivatives has not been achieved up to the present time. One of the important causes of the low yields of lepidine bases in the Beyer reaction is the great activity of formaldehyde, which gives a number of side products, including an aminomethylated aromatic nucleus. In the course of synthesizing lepidine and its derivatives by this method, we satisfied ourselves that addition of amine salt increases the yield of quinolinic base by at least 50%. It should be noted that the amino ketones,which appear to be intermediate products in the Beyer reaction [7], form unstable compounds with arylamines [8] which, are cyclized when they decompose. This mechanism for the Beyer reaction leads to the conclusion that while it is being carried out, it is expedient to have an excess of the reacting amine in the reaction mixture for possibly a more prolonged time. It was shown to be beneficial to introduce acetylated amines into the reaction as starting materials, since, as is well known, this diminishes the mobility of the hydrogens of the aromatic nucleus and makes more difficult the formation of substitution products,and thereby facilitates the cyclization reaction.

As a result of the experiments carried out, higher yields were achieved than by the Beyer method [4]. It was established that our method can be employed to obtain various lepidine derivatives; for example, by introducing methylethyl ketone into the reaction, the comparatively slightly accessible 3,4-dimethylquinolines are formed. Amines which are disubstituted in the aromatic nucleus give higher yields of quinolines.

The reaction mechanism, with reference to lepidine, is basically as follows [9]:



EXPERIMENTAL

Initially the experiments were set up to obtain lepidine and 6-methyllepidine from anhydroformaniline and anhydroformtoluidine. These experiments showed that addition of ferric chloride to the reaction increased the lepidine yield. It was then established that upon the addition of the hydrochlorides of the corresponding amine, the yield was increased at least 50%. Thus, lepidine is formed from anhydroformaniline in a yield of 6-8% of the theoretical, while by the addition of aniline hydrochloride (better in a total quantity of 2 moles of amine per 1 mole of anhydro-base) the yield was increased to 12%. 4,6-Dimethylquinoline can be obtained from p-toluidine in this way in a yield of 18% of the theoretical. The base was purified by decomposing the sulfate. The following method of preparing lepidine and its derivatives was subsequently worked out.

Synthesis of Lepidine

20 g of acetanilide, 20 ml of acetone, 30 ml of alcohol, 25 g of $FeCl_3 \cdot 6H_2O$ and 5 ml of concentrated hydrochloric acid were placed in a round-bottomed flask. The flask was supplied with a reflux condenser and a dropping funnel with an alcoholic solution of paraformaldehyde.* The mixture was heated to boiling and the solution was added from the dropping funnel over a period of 40 minutes. After this, the mixture was boiled for 20-25 minutes more, 5 ml of concentrated hydrochloric acid was added to the reaction flask, and the contents of the flask were boiled for an additional 30 minutes. After distilling off the alcohol, acetone, acetic acid and ethyl acetate at a temperature up to 100-105° (the bulb of the thermometer was submerged in the boiling reaction mixture) and rendering the mixture alkaline with concentrated sodium hydroxide solution, the base was steam distilled off.

The lepidine was purified from the aniline by means of diazotization or boiling a mixture of the ether-extracted base with 5 ml of acetic anhydride, with subsequent steam distillation. The yield of lepidine, with b.p. 258-263°, was 3.9 g (18.4%). Lepidine picrate melted at 212°. A mixed sample with known lepidine picrate did not display melting point depression.

Synthesis of 4,6-Dimethylquinoline

4,6-Dimethylquinoline, prepared from 20 g of p-acetyltoluidine, analogously to the preceding, was isolated in a quantity of 5.2 g (24.8%), with b.p. 263-270°. The picrate melted at 237°.

Synthesis of 4,6,8-Trimethylquinoline

20 g of aceto-m-xylidide, 20 ml of acetone, 30 ml of alcohol, 25 g of $FeCl_3 \cdot 6H_2O$ and 8 ml of concentrated hydrochloric acid (d 1.19) were placed in a round-bottomed flask. The mixture was heated to boiling and through a dropping funnel, inserted in a reflux condenser, a solution of 5 g of paraform in 30 ml of aclohol was continuously added dropwise over a period of 50 minutes. The mixture was boiled for 20 minutes more, after which 5 ml of concentrated hydrochloric acid was added to the flask and the boiling was continued for an hour. After cooling, the mixture was rendered alkaline with 40% sodium hydroxide solution, 30 ml of alcohol was added, and the iron hydroxide which settled out was filtered off. The filtrate was diluted with water to a volume of 400 ml, and the base which was evolved was extracted with ether. The ether was distilled off, the 215-310° fraction was collected, boiled with 100 ml of 15% hydrochloric acid to saponify unreacted aceto-m-xylydide. A saturated solution of potassium ferrocyanide was added to the hydrochloric acid solution of the bases until no more precipitate settled out. The precipitate was filtered off and decomposed with alkali, and the oil which was evolved was extracted with ether. After distilling off the ether, the base was fractionally distilled in the 270-280° range in a quantity of 7 g (33%); m.p. 51°. After recrystallization from a small quantity of petroleum ether, the m.p. was 57°. The picrate, precipitated from alcohol, had m.p. 209°.

0.1030 g sub.: 13 ml N_2 (21°, 754 mm). Found %: N 14.19. $C_{12}H_{13}N \cdot C_6H_2(NO_2)_3OH$. Calculated %: N 14.00.

The dichromate salt of the base was precipitated in the form of fine yellow needles.

0.1495 g sub.: 0.0412 g Cr_2O_3. Found %: Cr_2O_3 27.55. Calculated %: Cr_2O_3 27.14.

SUMMARY

1. Lepidine, 6-methyllepidine and 6,8-dimethyllepidine, which was hitherto undescribed in the literature, were prepared by acetylation of aromatic amines, formaldehyde and acetone in alcoholic solution in the presence of ferric

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* 6 g of paraformaldehyde was placed in an ampoule, 35 ml of ethyl alcohol and 2-3 drops of hydrochloric acid (d 1.19) were added, the ampoule was sealed, and the contents heated on a water bath until the paraform dissolved.

chloride in yields, respectively of 18%, 25% and 33%.

2. A method which was worked out for the synthesis of lepidine and its derivatives and which requires comparatively little time (4-5 hours) can be recommended as a preparative method for obtaining them.

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* See Consultants Bureau Translation, page 2257.

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CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXIV. CATALYTIC SYNTHESIS OF 2-(p-METHYLPHENYL)-QUINOLINE AND ITS DERIVATIVES

N. S. Kozlov and N. I. Panova

A new method of synthesizing α-phenyl derivatives of quinoline via the joint condensation ofan aromatic amine and an aromatic aldehyde with acetylene in the presence of copper or mercury salts [1] was described earlier in the work of one of us. A mechanism for this reaction was also then proposed and has been confirmed by our present work. The method proposed is a new method of synthesizing various derivatives of α-phenylquinoline themselves if various aromatic amines and aldehydes are introduced in the reaction.

Up to the present time, the following aromatic aldehydes have been introduced in the reaction of joint condensation of an aromatic amine and an aromatic aldehyde with acetylene: benzaldehyde, anisaldehyde and piperonal [2]. In the present work, the catalytic condensation of acetylene with various aromatic amines and p-toluyl aldehyde was studied. The following aromatic amines were studied: aniline, p-toluidine, p-anisidine and p-phenetidine. As a result of the work which we have carried out, 2-(p-methylphenyl)-quinoline and a number of its derivatives have been synthesized; these compounds had not been described in the literature and were prepared by us for the first time.

EXPERIMENTAL

Synthesis of 2-(p-Methylphenyl)-quinoline

Acetylene was passed into a reaction mixture consisting of 23 g of aniline, 18 g of p-toluyl aldehyde, 50 ml of alcohol and 5 g of mercuric chloride until the mixture was saturated. 2 g more of mercuric chloride was then introduced, and the saturation continued until cessation of acetylene absorption. About 20 hours were required for this. A 10% sodium hydroxide solution was then introduced into the reaction mass until it had an alkaline reaction and the alcohol and aromatic amine which had not entered into the reaction were steam distilled off. The reaction product consisted of a solid, resinous substance with a brown color. The following fractions were obtained by vacuum distilling it at 2.5 mm: 1st 80-150°, 3 g; 2nd 150-190°, 8 g; residue 10 g.

The second fraction crystallized on cooling; 5 g of a crystalline substance was obtained which had a m.p. of 81-82° after recrystallization from alcohol.

The yield of 2-(p-methylphenyl)-quinoline amounted to 15.2% of the aldehyde taken.

0.0854, 0.0957 g sub.: 4.04, 4.43 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.62, 6.48. $C_{16}H_{13}N$. Calculated %: N 6.39.

The substance obtained formed a picrate with a m.p. of 197-198° (with decomposition), and a platinate.

0.1038 g sub.: 0.240 g Pt. Found %: Pt 23.12. $(C_{16}H_{13}N)_2 \cdot H_2PtCl_6$. Calculated %: Pt 23.01.

Synthesis of 6-Methyl-2-(p-methylphenyl)-quinoline

28.0 g of p-toluidine was taken. The rest of the reagents were taken in the same quantities as indicated above. The isolation of the reaction products was carried out in the same way as in the preceding experiment. The reaction product consisted of a resinous substance. The following fractions were obtained by its vacuum distillation at 2.5 mm: 1st 90-150°, 2 g; 2nd 150-200°, 9 g; residue 9 g.

The second fraction crystallized on cooling. 6.0 g of a crystalline substance was obtained which had a m.p. of 137-138° after recrystallization from alcohol.

0.0968, 0.1263 g sub.: 4.23, 5.41 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 6.12, 5.99. $C_{17}H_{15}N$. Calculated %: N 6.00.

The substance obtained formed a picrate with a m.p. of 200-201°, and a platinate.

0.0950 g sub.: 0.213 g Pt. Found %: Pt 22.42. $(C_{17}H_{15}N)_2 \cdot H_2PtCl_6$. Calculated %: Pt 22.27.

The yield of 6-methyl-2-(p-methylphenyl)-quinoline amounted to 17.1% of the aldehyde taken.

Synthesis of 6-Methoxy-2-(p-methylphenyl)-quinoline

It was prepared from 30 g of p-anisidine by the method described above. The reaction product consisted of a resinous substance. Distillation at 2.5 mm yielded the following fractions: 1st 80-180°, 3 g; 2nd 180-230°, 10 g; residue 10 g.

7.7 g of a crystalline substance was obtained from the second fraction on cooling, which after recrystallization from alcohol had a m.p. of 150-151°.

0.1150, 0.1130 g sub.: 4.53, 4.56 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.51, 5.65. $C_{17}H_{15}ON$. Calculated %: N 5.62.

The substance obtained formed a picrate with a m.p. of 207-208°, and a platinate.

0.1020 g sub.: 0.016 g Pt. Found %: Pt 21.17. $(C_{17}H_{15}ON)_2 \cdot H_2PtCl_6$. Calculated %: Pt 21.48.

The yield of 6-methoxy-2-(p-methylphenyl)-quinoline was 20.6% of the aldehyde taken.

Synthesis of 6-Ethoxy-2-(p-methylphenyl)-quinoline

25 g of p-phenetidine was condenser with 15 g of p-toluyl aldehyde and acetylene under the conditions described above. By distillation of the resinous substance obtained in a vacuum at 2.5 mm the following fractions were obtained: 1st 90-140°, 3 g; 2nd 150-210°, 10 g; residue 9 g.

5 g of a crystalline substance was obtained by cooling the second fraction and had a m.p. of 138-139° after recrystallization from alcohol.

0.1792, 0.1046 g sub.: 6.74, 3.77 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 5.26, 5.04. $C_{18}H_{17}ON$. Calculated %: N 5.31.

The picrate with a m.p. of 191-192°, and a platinate, were formed.

0.1120 g sub.: 0.0231 g Pt. Found %: Pt 20.62. $(C_{18}H_{17}ON)_2 \cdot H_2PtCl_6$. Calculated %: Pt 20.84.

The yield of 6-ethoxy-2-(p-methylphenyl)-quinoline amounted to 15.2% of the aldehyde taken.

We, incidentally, prepared from p-toluyl aldehyde and a number of aromatic amines the Schiff bases, the m.p. of which were: 1) from p-toluidine 91-92°, 2) from p-phenetidine 105-107°; 3) from p-anisidine 86-87°.

SUMMARY

By joint catalytic condensation of acetylene and p-toluyl aldehyde with aniline, p-toluidine, p-anisidine and p-phenetidine, the following compounds: 2-(p-methylphenyl)-quinoline, 6-methyl-2-(p-methylphenyl)-quinoline, 6-methoxy-2-(p-methylphenyl)-quinoline and 6-ethoxy-2-(p-methylphenyl)-quinoline were prepared for the first time and described.

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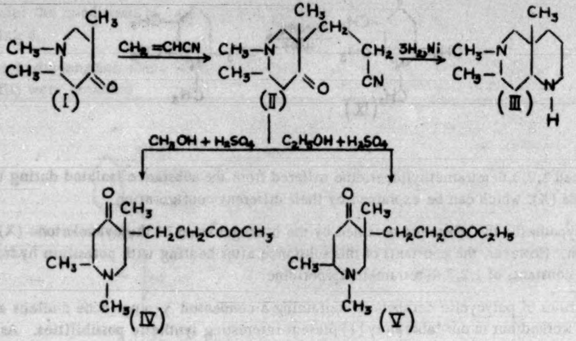
Molotov State Pedagogic Institute

CYANETHYLATION OF CYCLIC AND HETEROCYCLIC KETONES REDUCTION AND CYCLIZATION OF THE CYANETHYLATION PRODUCTS

I. N. Nazarov, G. A. Shvekhgeimer and V. A. Rudenko

In spite of the voluminous literature on the cyanethylation of various ketones, this reaction has hardly been studied at all for the heterocyclic ketones. The cyanethylation of γ-piperidones presents particular interest, since they have become readily available due to the works of our laboratory [1] and play an important role in the synthesis of valuable physiologically active compounds, in particular, of anesthetic substances.

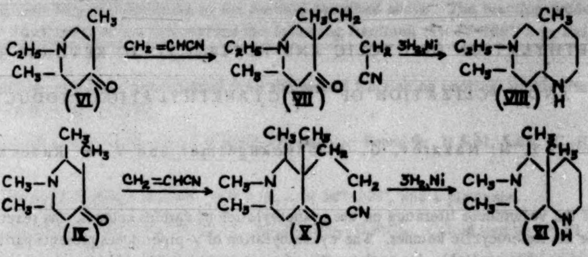
1,2,5-Trimethyl-5-(β-cyanethyl)-4-piperidone (II) was obtained in a yield of 90% by the reaction of acrylonitrile with excess 1,2,5-trimethyl-4-piperidone (I) for 24 hours at room temperature in the presence of small quantities of a 40% solution of potassium hydroxide. By hydrogenation in an autoclave at a temperature of 100° in the presence of Ni catalyst, the cyanethylated piperidone (II) was subjected to reduction cyclization, and formed trimethylperhydropyridopyridine (III) containing two condensed piperidine nuclei with an angular methyl group in a yield of 89%.



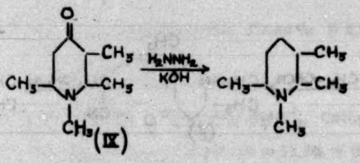
By heating the cyanethylated piperidone (II) with methyl and ethyl alcohols in the presence of sulfuric acid, the corresponding esters (IV) and (V) were obtained in a yield up to 75%.

By reaction of the cyanethylated piperidone (II) with methol alcohol a mixture of the initial cyanoketone (II) and the ketoester (IV) was obtained. Upon hydrogenation of this mixture the cyanoketone (II) was converted into the low-boiling perhydropyridopyridine (III), and after fractional distillation of the hydrogenation products the pure ketoester (IV) was successfully isolated.

Other γ-piperidones also behaved similarly in the cyanethylation reaction. Thus, for example, 1-ethyl-2,5-dimethyl-4-piperidone (VI) and 1,2,3,6-tetramethyl-4-piperidone (IX), upon cyanethylation, gave the corresponding cyanethyl derivatives (VII) and (X) in yields up to 90%, and upon hydrogenation of these last, the bicyclic compounds (VIII) and (XI) with two heterocyclic nitrogen atoms and an angular methyl group were obtained in a yield of 70-80%.



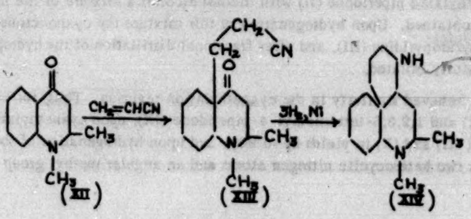
If the hydrogenation of the cyanoketone (X) is carried out at temperatures above 100°, in addition to the expected perhydropyridopyridine (XI) a considerable quantity of a low-boiling substance which corresponds in constants and analysis to piperidine with aggregate substituents amounting to C_4. One of these piperidines could be shown to be 1,2,3,6-tetramethylpiperidine. For comparison, we obtained the latter by reduction of the 1,2,3,6-tetramethyl-4-piperidone by Kishner's method:



The thus-obtained 1,2,3,6-tetramethylpiperidine differed from the substance isolated during the hydrogenation of the cyanoketone (X), which can be explained by their different configuration.

To verify this hypothesis, the substance obtained by the hydrogenation of the cyanoketone (X) was subjected to the Kizhner reaction. However, the constants of this substance after heating with potassium hydroxide again did not coincide with the constants of 1,2,3,6-tetramethylpiperidine.

The cyanethylations of polycyclic compounds containing a condensed γ-piperidone nucleus and readily obtained by the method worked out in our laboratory [1] present interesting synthetic possibilities. As an example, we accomplished the cyanethylation of 1,2-dimethyl-4-ketodecahydroquinoline (XII), during which the cyanethyl group enters into the angular position and forms the cyanethyl derivative (XIII) in a yield of 90%. Upon the hydrogenation of the latter, the tricyclic compound (XIV), containing two heterocyclic nitrogen atoms and a condensed ring in the angular position, was obtained in a yield of 81%.

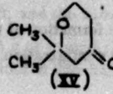


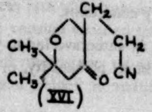
The structure of the cyanethylated ketone (XIII) was verified by a qualitative test for the formation of a formyl derivative [2] (presence of a free α-methylene group).

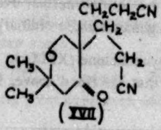
The angular structure of the ketone (XIII) is also a consequence of the fact that the cyclic ketones add acrylonitrile primarily to the tertiary carbon atom which has a substituent [3]. In accord with this the α-substituted cyclic ketones give high yields of monocyanethyl derivatives, while cyclic ketones which do not have substituents in the α-position readily form di- and tetracyanethylated products.

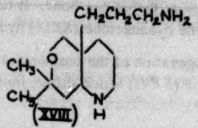
Upon the cyanethylation of 2,2-dimethyltetrahydro-4-pyrone (XV), the dicyanethyl derivative (XVII) was formed very readily, and only with a great excess of the ketone (XV) could the monocyanethylated product (XVI) be isolated successfully.

Upon the hydrogenation of the ketodinitrile (XVII) the bicyclic compound (XVIII) containing pyrane and piperidine rings was formed in a yield of 66%


(XV)


(XVI)

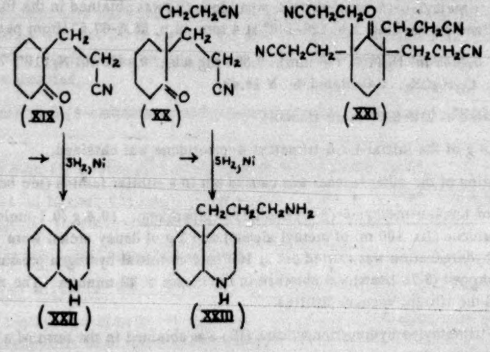

(XVII)


(XVIII)

Thus, one of the two α-methylenic groups in the ketone (XV) did not undergo cyanethylation; this is associated, in all probability, with the influence of the adjacent substituents (steric hindrance).

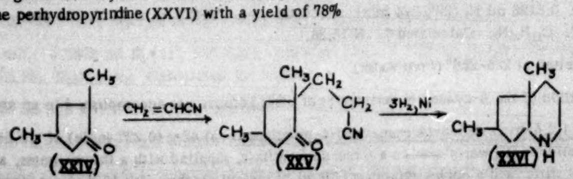
Upon the cyanethylation of cyclohexanone, as is well known, the tetracyanethyl derivative (XXI) is readily obtained, and under the conditions of excess ketone the mono- and dicyanethylated products (XIX) and (XX) were successfully isolated.

Upon the hydrogenation of the latter in the presence of Raney nickel under pressure the decahydroquinolines (XXII) and (XXIII) were obtained



(XIX) (XX) (XXI) (XXII) (XXIII)

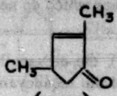
2,4-Dimethylcyclopentanone (XXIV) similarly to 2-methylcyclohexanone [4], readily adds one molecule of acrylonitrile and gives with a yield of 71% the monocyanethyl derivative (XXV). The latter is converted by hydrogenation into the perhydropyrindine (XXVI) with a yield of 78%



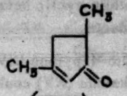
(XXIV) (XXV) (XXVI)

Upon the cyanethylation of the isomeric dimethylcyclopentenones (XXVII) and (XXVIII) the same monocyanethyl derivative (XXIX), corresponding to the ketone (XXVIII), is obtained in each case. Consequently, the ketone

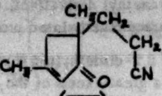
(XXVII) is isomerized under the conditions of the cyanethylation reaction (under the influence of alkali) into the ketone (XXVIII), as had been previously established by Nazarov and Elizarova [5].



(XXVII)



(XXVIII)



(XXIX)

An attempt was made to convert the unsaturated cyanoketone (XXIX) into the saturated cyanoketone (XXV) via hydrogenation of the double bond. It turned out that neither over palladium nor over platinum catalysts was the double bond in the cyanoketone (XXIX) hydrogenated under ordinary conditions.

The hydrogenation of the unsaturated cyanoketone (XXIX) in an autoclave led to the formation of the isomeric perhydropyrindine (XXVI) which differs from that described above, in all probability, in its configuration.

EXPERIMENTAL

I. Reaction of Acrylonitrile With 1,2,5-Trimethyl-4-piperidone

A mixture of 50 g (0.35 mole) of 1,2,5-trimethyl-4-piperidone (I) and 3 g of a 40% aqueous solution of potassium hydroxide was placed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 7 g (0.13 mole) of acrylonitirile was gradually added during energetic stirring and cooling with cold water at such a rate that the temperature of the mixture did not rise above 20°. After the addition of acrylonitrile, the sitrring was continued for 6 hours at room temperature, and then the mixture was left for 48 hours. The alkali was neutralized with an equivalent quantity of concentrated hydrochloric acid, the potassium chloride which precipitated was filtered off and the filtrate was vacuum distilled.

23.1 g of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II) was obtained in the form of a thick yellow oil which rapidly crystallized on standing; b.p. 138-140° at 4 mm; m.p. 66.5-67.5° (from petroleum ether).

3.600 mg sub.: 0.4645 ml N_2 (19°, 738 mm). 3.380 mg sub.: 0.4400 ml N_2 (19°, 736 mm). Found %: N 14.65, 14.73. $C_{11}H_{18}ON_2$. Calculated %: N 14.43.

The picrate melted at 212-213° (from alcohol).

In addition, 28.4 g of the initial 1,2,5-trimethyl-4-piperidone was obtained.

The cyanethylation of the other ketones was carried out in a similar fashion (see below).

Hydrogenation of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone. 19.4 g (0.1 mole) of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II), 100 ml of methyl alcohol and 1 g of Raney nickel were placed in a 250 ml rotating autoclave. The hydrogenation was carried out at 100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (6.75 liters) was absorbed in the course of 40 minutes. The mixture was cooled, the nickel filtered off and the filtrate vacuum distilled.

16.2 g of 6,7,9-trimethylperhydropyridopyridine (III) was obtained in the form of a colorless, mobile liquid with a characteristic amine odor:

B.p. 71-73.5° at 3 mm; n_D^{20} 1.4933; d_4^{20} 0.9576; MR_D 56.31; calculated 56.14.

2.265 mg sub.: 0.3126 ml N_2 (22°, 724 mm). 4.030 mg sub.: 0.5473 ml N_2 (20°, 723 mm). Found %: N 15.21, 15.07. $C_{11}H_{22}N_2$. Calculated %: N 15.38.

The picrate melted at 255-256° (from water).

The hydrogenation of the β-cyanethyl derivatives of other ketones was accomplished in an analogous fashion.

Alcoholysis of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone. a) 42 g (0.227 mole) of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone (II) was placed in a three-necked flask, supplied with a thermometer, a reflux condenser and a mechanical stirrer, and a cooled mixture of 80 ml of methyl alcohol with 45 g of concentrated sulfuric acid was added. The reaction mass was stirred for 10 hours at 74°, and after cooling was poured out into 300 ml of water. The excess sulfuric acid was neutralized with soda; the base was salted out with potash. The upper layer was separated, while the aqueous layer was extracted with ether 5 times. The ethereal extracts were combined and dried with calcined sodium sulfate. The ether was distilled off and the residue vacuum distilled.

41.4 g of a mixture of the initial cyanoketone (II) and the piperidine ester (IV) was obtained in the form of a light yellow oil which crystallized on standing; b.p. 123-129° at 4 mm.

The cyanoketone (II) isolated from this mixture melted at 67-69° (from petroleum ether) and yielded no depression with the initial substance.

To isolate the piperidine ester (IV) in the pure form the mixture obtained was subjected to hydrogenation with the object of freeing it from the initial cyanoketone (II). 25 g of the above-described mixture of substances (II) and (IV), 100 ml of methyl alcohol and 1 g of Raney nickel were placed in a 250 ml rotating autoclave. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 120 atm. After 1 hour 30 atm. of hydrogen had been absorbed, after which the rate of hydrogenation sharply diminished. The autoclave was cooled, the nickel filtered off, and the filtrate vacuum distilled three times.

10.5 g of trimethylperhydropyridopyridine (III) was isolated with a b.p. of 76-78° at 3.5 mm, the picrate of which melted at 255-256° and yielded no melting point depression with the sample described above.

In addition, 12.2 g of 1,2,5-trimethyl-5-(β-carbomethoxyethyl)-4-piperidone (IV) was obtained in the form of a colorless oil:

B.p. 117-119° at 5 mm; n_D^{20} 1.4703; d_4^{20} 1.0390; MR_D 60.99; calculated 61.02.

4.720 mg sub.: 11.030 mg CO_2; 3.900 mg H_2O. 5.563 mg sub.: 13.027 mg CO_2; 4.700 mg H_2O. Found %: C 63.77, 63.90; H 9.46, 9.42. $C_{12}H_{21}O_3N$. Calculated %: C 63.44. H 9.25.

The picrate melted at 204-205° (from water).

The ester (IV) obtained yielded an intense raspberry coloration with sodium nitroprusside in alkaline medium (test for the carbonyl group) [6].

b) A mixture of 20 g (0.1 mole) of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone, 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred for 20 hours at 90-92° (boiling point of the mixture). The cooling reaction mass was decomposed with 100 ml of water. The acid was neutralized with soda, the base was salted out with potash (a stable emulsion was formed), the mixture was repeatedly extracted with ether, dried with calcined sodium sulfate and vacuum distilled.

18.9 g of 1,2,5-trimethyl-5-(β-carboethoxyethyl)-4-piperidone (V) (75%) was obtained in the form of a colorless oil:

b.p. 117-118° at 3.5 mm; n_D^{20} 1.4682; d_4^{20} 1.0208; MR_D 65.65; calculated 65.64.

5.772 mg sub.: 0.314 ml N_2 (24°, 731 mm). 4.829 mg sub.: 0.255 ml N_2 (23°, 743 mm). Found %: N 5.99, 5.96. $C_{13}H_{23}O_3N$. Calculated %: N 5.81.

The picrate melted at 200.5-201° (from moist acetone).

II. Reaction of Acrylonitrile With 1-Ethyl-2,5-dimethyl-4-piperidone

200 g (1.3 mole) of 1-ethyl-2,5-dimethyl-4-piperidone (VI), 5 g of a 40% solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken for the reaction.

71.6 g of 1-ethyl-2,5-dimethyl-5-(β-cyanethyl)-4-piperidone (VII) was obtained in the form of a viscous yellow oil.

B.p. 155-158° at 7 mm; n_D^{20} 1.4835; d_4^{20} 1.0040; MR_D 59.22; calculated 59.18.

3.000 mg sub.: 0.3568 ml N_2 (21°, 735 mm). 2.880 mg sub.: 0.3438 ml N_2 (21°, 735 mm). Found %: N 13.24, 13.28. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

The picrate melted at 177-178° (from acetone).

100 g of the initial 1-ethyl-2,5-dimethyl-4-piperidone (VI) was recovered from the experiment.

Hydrogenation of 1-ethyl-2,5-dimethyl-5-(β-cyanethyl)-4-piperidone. 36.5 g (0.175 mole) of 1-ethyl-2,5-dimethyl-5-(β-cyanethyl)-4-piperidone (VII), 115 g of methyl alcohol and 2 g of Raney nickel were taken. The hydrogenation was carried out at 80-95° and an initial hydrogen pressure of 140 atm. The theoretical quantity of hydrogen (11.8 liters) was absorbed in the course of 1.5 hour.

25 g of 6-ethyl-7,9-dimethylperhydropyridopyridine (VIII) was obtained; it consisted of a colorless oil with a characteristic amine odor:

b.p. 90-94° at 5 mm; n_D^{20} 1.4917; d_4^{20} 0.9464; MR_D 60.05; calculated 60.41.

4.425 mg sub.: 0.5528 ml N_2 (22°, 724 mm). 5.235 mg sub.: 0.6697 ml N_2 (23°, 723 mm). Found %: N 14.21, 14.04. $C_{12}H_{24}N_2$. Calculated %: N 14.28.

The hydrochloride with a m.p. of 211.5-212° (from alcohol) was obtained.

III. Reaction of Acrylonitrile With 1,2,3,6-Tetramethyl-4-piperidone

135 g (0.87 mole) of 1,2,3,6-tetramethyl-4-piperidone (IX), 9 g of a 40% aqueous solution of potassium hydroxide and 15 g (0.28 mole) of acrylonitrile were taken inthe reaction. After the addition of acrylonitrile, the mixture was heated for 1 hour at 70-75° and then was left for 48 hours.

42 g of 1,2,3,6-tetramethyl-3-(β-cyanethyl)-4-piperidone (X) was obtained in the form of a thick yellow oil:

b.p. 142-145° at 1 mm; n_D^{20} 1.4852; d_4^{20} 1.0183; MR_D 58.56; calculated 58.50.

3.450 mg sub.: 0.4158 ml N_2 (20°, 723 mm). 4.230 mg sub.: 0.5214 ml N_2 (20°, 718 mm). Found %: N 13.35, 13.57. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

The picrate melted at 196-197° (from acetone).

92.5 g of the initial 1,2,3,6-tetramethyl-4-piperidone (IX) was recovered from the experiment.

Hydrogenation of 1,2,3,6-tetramethyl-3-(β-cyanethyl)-4-piperidone. a) 22 g (0.105 mole) of 1,2,3,6-tetramethyl-3-(β-cyanethyl)-4-piperidone (X), 130 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 85-90° and an initial hydrogen pressure of 110 atm. The theoretical quantity of hydrogen (7.1 liters) was absorbed in the course of 30 minutes.

17 g of 6,7,8,9-tetramethylperhydropyridopyridine (XI), a colorless liquid with a characteristic amine odor, was obtained:

b.p. 97-101° at 4 mm; n_D^{20} 1.4988; d_4^{20} 0.9622; MR_D 60.76; calculated 60.41.

2.915 mg sub.: 0.3695 ml N_2 (23°, 272 mm). 4.115 mg sub.: 0.5282 ml N_2 (24°, 716 mm). Found %: N 13.98, 14.09. $C_{12}H_{24}N_2$. Calculated %: N 14.28.

The hydrochloride melted at 140-142.5°.

In addition, 1.1 g of a substance with a b.p. of 58-60° at 11 mm; n_D^{20} 1.4553 was obtained (see below).

b) 12.5 g (0.06 mole) of the ketonitrile (X), 100 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 100-120° and an initial hydrogen pressure of 120 atm. 54 atm of hydrogen was absorbed in the course of 1 hour (30 atm was theoretically required for the reduction cyclization).

3.5 g of the above described 6,7,8,9-tetramethylperhydropyridopyridine (XI) with a b.p. of 122-125° at 10 mm; n_D^{20} 1.4989 was obtained.

In addition, 4.9 g of a substance agreeing in analysis with 1,2,3,6-tetramethylpiperidine was obtained in the form of a colorless, mobile liquid with a sharp amine odor:

b.p. 32-33° at 3 mm; 184-189° at 761 mm; n_D^{20} 1.4549; d_4^{20} 0.8506.

5.760 mg sub.: 0.4792 ml N_2 (18°, 743 mm). 4.635 mg sub.: 0.3911 ml N_2 (19°, 743 mm). 3.670 mg sub.: 0.3273 ml N_2 (23°, 729 mm). Found %: N 9.54, 9.64, 9.86. $C_9H_{19}N$. Calculated %: N 9.93.

The hydrochloride melted at 145-146° (from acetone). The picrate was not successfully isolated in the crystalline form.

By heating this substance (3 g) with potassium hydroxide in 1,3-butylene glycol for 5.5 hours at 150-160° (under the conditions of Kizhner's reduction; see below), 2.1 g of base with a b.p. of 172-176° at 748 mm was obtained; its hydrochloride also melted at 145-146° and yielded no melting point depression with the preceding sample.

The picrate was not successfully isolated in the crystalline form.

Reduction of 1,2,3,6-tetramethyl-4-piperidone by Kizhner's method. A mixture of 15.5 g (0.1 mole) of 1,2,3,6-tetramethyl-4-piperidone (XI), 75 ml of 1,3-butylene glycol, 18 g of powdered potassium hydroxide and 15 g of hydrazine hydrate was heated with a reflux condenser for 2.5 hours at 148-150°. An energetic evolution of gas bubbles and a darkening of the mixture were observed. After this the reflux condenser was replaced by a headpiece in which a thermometer was placed so that the bulb was deeply immersed in the liquid. The lead off of the headpiece was joined with a straight condenser and a small quantity of liquid was distilled off at a temperature of 180°. Then the headpiece was replaced by the reflux condenser and the mixture was heated for 3 hours at 180-195°. The mixture was cooled, the reflux condenser was again replaced by the headpiece and all the substance was distilled off which boiled below 190°. Both distillates were combined and saturated with potash; the upper layer was separated while the lower layer was twice extracted with ether.

The product was dried with fused sodium hydroxide and distilled. 9.3 g (66%) of 1,2,3,6-tetramethylpiperidine was obtained; it consisted of a colorless, mobile liquid with a sharp piperidine odor:

b.p. 161-163° at 748 mm; 48-49.5° at 11 mm; n_D^{20} 1.4531; d_4^{20} 0.8407; MR_D 45.34; calculated 45.50.

3.395 mg sub.: 0.289 ml N_2 (22°, 757 mm). 3.115 mg sub.: 0.269 ml N_2 (22°, 758 mm). Found %: N 9.77, 9.98. $C_9H_{19}N$. Calculated %: N 9.93.

The picrate with a m.p. of 210.5-211° (from alcohol) was obtained. The hydrochloride could not be obtained in the crystalline form.

IV. Reaction of Acrylonitrile With 1,2-Dimethyldecahydro-4-quinolone

38 g (0.210 mole) of 1,2-dimethyldecahydro-4-quinolone (XII), 1.2 g of a 40% aqueous solution of potassium hydroxide and 3.5 g (0.066 mole) of acrylonitrile were taken.

14 g of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone (XIII) was obtained; it consisted of a light orange, viscous oil; b.p. 166-170° at 2 mm; n_D^{20} 1.5069; d_4^{20} 1.0608; MR_D 65.63; calculated 66.22.

6.419 mg sub.: 0.684 ml N_2 (18°, 751 mm). 6.510 mg sub.: 0.711 ml N_2 (20°, 744 mm). Found %: N 12.20, 12.35. $C_{14}H_{22}ON_2$. Calculated %: N 11.96.

The picrate melted at 197-197.5° (from a mixture of moist acetone and alcohol).

15.9 g of the initial 1,2-dimethyldecahydro-4-quinolone (XII) was recovered from the experiment.

Hydrogenation of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone. 15 g (0.064 mole) of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone (XIII), 135 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (4.3 liters) was absorbed in the course of 30 minutes.

12.4 g of a substance (XIV) was obtained in the form of a colorless, viscous oil with a characteristic amine odor:

b.p. 134-138° at 5 mm; n_D^{20} 1.5262; d_4^{20} 1.0360; MR_D 65.80; calculated 66.69.

2.620 mg sub.: 0.3047 ml N_2 (24°, 729 mm). 3.695 mg sub.: 0.4282 ml N_2 (23°, 729 mm). Found %: N 12.84, 12.84. $C_{14}H_{26}N_2$. Calculated %: N 12.61.

The hydrochloride with a m.p. of 221-222° (from alcohol) was obtained.

Reaction of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone with benzaldehyde. 2.4 g (0.01 mole) of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone (XIII) was dissolved in 10 ml of ethyl alcohol. 4 ml of a 15% aqueous solution of sodium hydroxide, 1.2 ml of freshly prepared benzaldehyde and 1 ml of water were added to the solution. The solution became completely transparent while being stirred. After 15 minutes, the evolution of an oil began, which did not crystallize on standing even for a month. 1.3 g of a thick yellow oil was obtained by distillation, which did not crystallize on standing:

b.p. 135-195° (the bulk at 190-195°) at 0.015 mm.

Reaction of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone with ethyl formate. 0.23 g (0.01 mole) of finely divided metallic sodium, 2.34 g (0.01 mole) of 1,2-dimethyl-10-(β-cyanethyl)-decahydro-4-quinolone (XIII) and 30 ml of absolute ether were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a dropping funnel. 1.2 g (0.016 mole) of ethyl formate was added to the stirred mixture. The evolution of bubbles of gas was observed. The mixture was stirred for 3 hours and then left overnight. A brown precipitate settled out. The formylation product was not isolated, but was used for a qualitative reaction for a 1,3-dicarbonyl compound.

Qualitative test for a 1,3-dicarbonyl compounds [2]. 1.45 g (0.01 mole) of phenylhydrazine hydrochloride in 30 ml of water was gradually added to the formylation product while it was being stirred; the mixture evolved an appreciable amount of heat. After the spontaneous heat evolution of the mixture was ended, the ethereal layer was separated while the aqueous layer was twice extracted with ether. The ether was distilled off, the residue dissolved in 15 ml of ethyl alcohol. The alcoholic solution was placed in a round-bottomed-flask, joined with a reflux condenser, and the mixture was heated to boiling. 1.15 g (0.05 mole) of metallic sodium was gradually added to the boiling alcoholic solution. After solution of all the sodium the mixture was cooled and 30 ml of water was added. The alcohol was distilled off in a vacuum; an oil thereupon precipitated which was extracted three times with ether. The ether was distilled off and the residue dissolved in 10 ml of concentrated sulfuric acid. The solution obtained, when shaken with an aqueous solution of sodium nitrite, yielded a cherry red color and, on shaking with an aqueous solution of potassium bichromate, exhibited a blue-green coloration.

V. Reaction of Acrylonitrile With 2,4-Dimethylcyclopentanone

110 g (1 mole) of 2,4-dimethylcyclopentanone (XXIV) (b.p. 74-76° at 45 mm; n_D^{20} 1.4319), 8 g of a 40% aqueous solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken.

44 g of 2,4-dimethyl-2-(β-cyanethyl)-cyclopentanone (XXV) was obtained in the form of a colorless oil:

b.p. 109.5-110° at 3.5 mm; n_D^{20} 1.4617; d_4^{20} 0.9851; MR_D 46.02; calculated 46.01.

5.690 mg sub.: 0.421 ml N_2 (20°, 749 mm). 9.055 mg sub.: 0.677 ml N_2 (20°, 749 mm). Found %: N 8.49, 8.38. $C_{10}H_{15}ON$. Calculated %: N 8.48.

72.8 g of the initial 2,4-dimethylcyclopentanone (b.p. 71-73° at 43 mm; n_D^{20} 1.4316) was recovered from the experiment.

Hydrogenation of 2,4-dimethyl-2-(β-cyanethyl)-cyclopentanone. 25 g (0.15 mole) of 2,4-dimethyl-2-(β-cyanethyl)-cyclopentanone (XXV), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (10 liters) was absorbed in the course of 45 minutes.

18 g of 4a,6-dimethylperhydropyrindine (XXVI) was obtained; it consisted of a colorless, mobile liquid with a sharp amine odor:

b.p. 67-69° at 8 mm; n_D^{20} 1.4751; d_4^{20} 0.8975; MR_D 48.00; calculated 47.58.

5.720 mg sub.: 0.455 ml N_2 (18°, 753 mm). 7.285 mg sub.: 0.591 ml N_2 (22°, 744 mm). Found %: N 9.20, 9.20. $C_{10}H_{19}N$. Calculated %: N 9.15.

The hydrochloride with a m.p. of 143-144° (from acetone) was obtained.

VI. Reaction of Acrylonitrile With 2,4-Dimethyl-Δ^4-cyclopentenone

70 g (0.64 mole) of 2,4-dimethyl-Δ^4-cyclopentenone (XXVII), 5 g of a 40% aqueous solution of potassium hydroxide and 35 g (0.66 mole) of acrylonitrile were taken in the reaction.

25.1 g of 2,4-dimethyl-2-(β-cyanethyl)-Δ^4-cyclopentenone (XXIX) was obtained in the form of a colorless viscous oil:

b.p. 118-122° at 5.5 mm; n_D^{20} 1.4760; d_4^{20} 1.0353; MR_D 44:46; calculated 45.54; $^{E}MR_D$ 1.08.

6.515 mg sub.: 1.97 ml (0.02 N hyposulfite). 10.358 mg sub.: 3.15 ml (0.02 N hyposulfite). Found %: N 8.55; 8.59. $C_{10}H_{13}ON$. Calculated %: N 8.59.

2,4-Dinitrophenylhydrazone melted at 109.5-111° (from methanol).

28 g of the initial 2,4-dimethyl-Δ^4-cyclopentenone (b.p. 179-182°; n_D^{20} 1.4758) was recovered from the experiment.

The substance obtained did not appear to be homogeneous. On shaking it with hydrogen in the presence of Pd- and Pt catalysts, hydrogenation did not occur, but after distillation, a pure substance was isolated:

b.p. 110.5-111° at 4.5 mm; n_D^{20} 1.4759; d_4^{20} 1.0834; MR_D 44.48; calculated 45.54; $^{E}MR_D$ 1.06.

3.545 mg sub.: 9.447 mg CO_2; 2.585 mg H_2O. 4.510 mg sub.: 12.027 mg CC_2; 3.305 mg H_2O. Found %: C 72.72, 72.77; H 8.11, 8.20. $C_{10}H_{13}ON$. Calculated %: C 73.62; H 7.97.

The 2,4-dinitrophenylhydrazone of this cyanoketone melted at 162.5-164°, and then solidified and again melted at 176-179° (from methanol).

Hydrogenation of 2,4-dimethyl-2-(β-cyanethyl)-Δ^4-cyclopentenone. 20 g (0.12 mole) of 2,4-dimethyl-2-(β-cyanethyl-)-Δ^4-cyclopentenone (XXIX), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 125 atm. The theoretical quantity of hydrogen (10.8 liters) was absorbed in the course of 2 hours.

4.5 g of the isomeric 4a,6-dimethylperhydropyrindine (XXVI) was obtained; it consisted of a colorless, mobile liquid with a sharp amine odor:

b.p. 69-71° at 9 mm; n_D^{20} 1.4757; d_4^{20} 0.9083; MR_D 47.48; calculated 47.58.

4.090 mg sub.: 0.3215 ml N_2 (19°, 741 mm). 3.280 mg sub.: 0.2617 ml N_2 (19°, 741 mm). Found %: N 8.93, 9.09. $C_{10}H_{19}N$. Calculated %: N 9.15.

The hydrochloride was prepared and had a m.p. of 226-227° (from an acetone alcohol mixture).

VII. Reaction of Acrylonitrile With 2,4-Dimethyl-Δ^2-cyclopentenone

83 g (0.75 mole) of 2,4-dimethyl-Δ^2-cyclopentenone (XXVIII) (b.p. 48-50° at 8 mm; n_D^{20} 1.4664), 2 g of a 40% aqueous solution of potassium hydroxide and 15 g (0.28 mole) of acrylonitrile were taken in the reaction. The reaction was carried out for 6 hours at a temperature of 20-30°.

5.5 g of 2,4-dimethyl-2-(β-cyanethyl)-Δ^4-cyclopentenone (XXIX) was obtained in the form of a thick colorless oil:

b.p. 110-117° at 3.5 mm; n_D^{20} 1.4768; d_4^{20} 1.0345; MR_D 44.71; calculated 45.54; EMR_D 0.83.

The 2,4-dinitrophenylhydrazone melted at 178-180° (from methanol) and gave no melting point depression with the preceding sample.

68 g of the initial 2,4-dimethyl-Δ^2-cyclopentenone (b.p. 48-49° at 8 mm; n_D^{20} 1.4659) was recovered from the experiment.

VIII. Reaction of Acrylonitrile With 2,2-Dimethyltetrahydro-4-pyrone

a) 185 g (1.445 mole) of 2,2-dimethyltetrahydro-4-pyrone (XV), 12 g of a 40% aqueous solution of potassium hydroxide and 20 g (0.38 mole) of acrylonitrile were taken in the reaction.

17.8 g of monocyanethylated 2,2-dimethyletetrahydro-4-pyrone (XVI) was obtained; it consisted of a thick, light yellow oil:

b.p. 132-136° at 5 mm; 124-126° at 4 mm; n_D^{20} 1.4735; d_4^{20} 1.0601; MR_D 47.94; calculated 47.65.

11.20 mg sub.: 27.36 mg CO_2; 8.76 mg H_2O. 10.71 mg sub.: 26.07 mg CO_2; 8.35 mg H_2O. Found %: C 66.66, 66.43; H 8.75, 8.71. $C_{10}H_{15}O_2N$. Calculated %: C 66.30; H 8.29.

In addition, 44.7 g of dicyanethylated 2,2-dimethyltetrahydro-4-pyrone (XVII) was obtained; it consisted of a crystalline white mass, m.p. 105.5-106.5° (from alcohol).

4.495 mg sub.: 0.470 ml N_2 (20°, 760 mm). 5.139 mg sub.: 0.633 ml N_2 (20°, 760 mm). Found %: N 12.18, 12.11. $C_{13}H_{18}O_2N_2$. Calculated %: N 11.96.

b) 117 g (0.9 mole) of the ketone (XV), 15 g of a 40% aqueous potassium hydroxide solution, 96 g (1.8 mole) of acrylonitrile and 100 ml of dioxane were taken in the reaction.

161 g of dicyanethylated product (XVII) with a m.p. of 103.5-105.5° (from alcohol) was obtained. A mixed sample with the substance obtained from experiment a) yielded no depression.

Hydrogenation of 2,2-dimethyl-5,5-di(β-cyanethyl)-tetrahydro-4-pyrone. 23.4 g (0.1 mole) of 2,2-dimethyl-5,5-di(β-cyanethyl)-tetrahydro-4-pyrone (XVII), 100 ml of methyl alcohol and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 90-110° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (11.2 liters) was absorbed in the course of 2 hours.

15.1 g of 7,7-dimethyl-9-(γ-aminopropyl)-perhydropyranopyridine (XVIII) was obtained; it consisted of a colorless viscous oil:

b.p. 130-134° at 4 mm; n_D^{20} 1.5149; d_4^{20} 1.0637; MR_D 64.06; calculated 66.50.

4.490 mg sub.: 0.4784 ml N_2 (19°, 735 mm). 5.085 mg sub.: 0.5499 ml N_2 (20°, 732 mm). Found %: N 12.07, 12.13. $C_{13}H_{26}ON_2$. Calculated %: N 12.34.

The hydrochloride, which melted at 229.5-231° with decomposition (from acetone) was obtained.

IX. Reaction of Acrylonitrile with Cyclohexanone

400 g (4 moles) of cyclohexanone, 30 g of a 40% aqueous potassium hydroxide solution and 106 g (2 moles) of acrylonitrile were taken in the reaction. The following fractions were obtained:

1) 2-(β-Cyanethyl)-cyclohexanone (XIX)—89 g, b.p. 127-129° at 8 mm [7]; 2) 2,2-di(β-cyanethyl)-cyclohexanone (XX)—54 g, b.p. 185-192° at 0.1 mm, m.p. 68-69° (from alcohol) [7].

38 g of crystalline tetra(β-cyanethyl)-cyclohexanone (XXI) was isolated from the residue; m.p. 164-165.5° (from a mixture of alcohol and acetone [7]).

243 g of cyclohexanone was recovered from the experiment.

Hydrogenation of 2-(β-cycanethyl)-cyclohexanone. 30.2 g (0.2 mole) of 2-(β-cyanethyl)-cyclohexanone (XIX), 100 ml of methyl alcohol and 2 g of Raney nickel were taken. Hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in the course of 1 hour.

19 g of the previously described [8] decahydroquinoline (XXII) with a b.p. of 74-75° at 9 mm; 204-205° at 756 mm; n_D^{20} 1.4927 was evolved.

The hydrochloride with a m.p. of 231.5-233° (from a mixture of acetone and alcohol) [8] was obtained.

Hydrogenation of 2,2-di-(β-cyanethyl)-cyclohexanone. 20.4 g (0.1 mole) of 2,2-di-(β-cyanethyl)-cyclohexanone (XX), 100 ml of methyl alcohol and 1 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° and an initial hydrogen pressure of 150 atm. The theoretical quantity of hydrogen (11.2 liters) was absorbed in the course of 45 minutes.

8.1 g of 10-(γ-aminopropyl)-decahydroquinoline (XXIII) was obtained; it consisted of a white crystalline mass with an amine odor; b.p. 114-120° at 4 mm; m.p. 42-43°. The hydrochloride with a m.p. of 296-298° (from moist alcohol) was prepared.

4.870 mg sub.: 0.431 ml N_2 (20°, 755 mm). 4.450 mg sub.: 0.394 ml N_2 (20°, 752 mm). Found %: N 10.28, 10.20. $C_{12}H_{26}N_2Cl_2$. Calculated %: N 10.40.

The picrate with a m.p. of 188.5-189.5° (from methyl alcohol) was prepared.

SUMMARY

1. The cyanethylation reaction was carried out with the following cyclic and heterocyclic ketones: cyclohexanone, 2,4-dimethylcyclopentanone, 2,4-dimethyl-Δ^4-cyclopentenone, 2,4-dimethyl-Δ^2-cyclopentenone, 2,2-dimethyltetrahydro-4-pyrone, 1,2,5-trimethyl-4-piperidone, 1,2,3,6-tetramethyl-4-piperidone, 1-ethyl-2,5-dimethyl-4-piperidone and 1,2-dimethyldecahydro-4-quinolone.

2. The ketones which have a substituent in the α-position: 2,4-dimethylcyclopentanone, 1,2,5-trimethyl-4-piperidone, 1,2,3,6-tetramethyl-4-piperidone, 1-ethyl-2,5-dimethyl-4-piperidone and 1,2-dimethyldecahydro-4-quinolone form monocyanethyl products in high yields; 2,2-dimethyltetrahydro-4-pyrone primarily forms a dicyanethylated product.

3. The same ketonitrile was obtained from 2,4-dimethyl-Δ^4-cyclopentenone and 2,4-Δ^2-cyclopentenone.

4. The ketonitriles and ketodinitriles obtained are cyclized by hydrogenation in an autoclave into the corresponding piperidine systems. The hydrogenation of 1,2,3,6-tetramethyl-3-(β-cyanethyl)-4-piperidone is accompanied by hydrogenolysis at temperatures above 100°.

5. The expected 1,2,5-trimethyl-5-(β-carboalkoxyethyl)-4-piperidones are formed in yields up to 75% by the alcoholysis of 1,2,5-trimethyl-5-(β-cyanethyl)-4-piperidone in methyl and ethyl alcohols.

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HYDROLYSIS, ALCOHOLYSIS AND HYDROGENATION OF β-CYANETHYL ETHERS OF GLYCOLS

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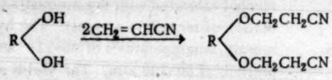
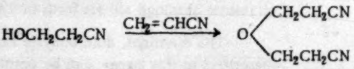
The addition reaction of acrylonitrile to substances having a "mobile" hydrogen atom (cyanethylation reaction), has acquired enormous significance for synthetic organic chemistry in the last few years. Introduction of the nitrile group gives rich possibilities for the synthesis of various classes of organic compounds. This explains the exceptionally great interest in the cyanethylation reaction, to the study of which numerous experimental works and also a number of literature reviews published in the course of the last five years [1] have been devoted.

Many valuable substances, which have found wide practical application, have been synthesized with the aid of the cyanethylation reaction. The addition products of acrylonitrile to glycols and ethylenecyanhydrin are particularly interesting. The di-(β-cyanethyl) ethers thus obtained are the starting materials for the synthesis of the corresponding diamines, dicarboxylic acids and their esters with oxygen heteroatoms in the basic carbon chain. These diamines, dicarboxylic acids and their esters can be used as intermediate products for the preparation of new synthetic fibers with increased hydrophilic qualities, plastics, and other valuable products.

The cyanethylation of glycols and of ethylene cyanhydrin has been quite well studied [1, 8]. This reaction proceeds readily with high yields under the action of alkaline catalysts



$$R(OH)_2 \xrightarrow{2CH_2=CHCN} R(OCH_2CH_2CN)_2$$



$$HOCH_2CH_2CN \xrightarrow{CH_2=CHCN} O(CH_2CH_2CN)_2$$

However, the further conversions of the di-(β-cyanethyl) ethers obtained have been insufficiently studied.

Alkaline hydrolysis was unsuitable for the saponification of the β-cyanethyl ethers into the corresponding carboxylic acids, in view of the fact that the addition products of acrylonitrile to alcohols and glycols are decomposed into the initial components by heating in the presence of alkali (reversibility of the cyanethylation reaction). Saponification of the β-cyanethyl ethers with the aid of concentrated hydrochloric acid [2] was, therefore, proposed.

The alcoholysis of the addition products of acrylonitrile to alcohols and glycols has hardly been described in the literature, with the exception of isolated patent data [3, 4], in which neither the conditions under which the reaction was carried out nor the yields of the ethers obtained were set forth.

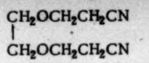
The hydrogenation of β-cyanethyl ethers into the corresponding amines has been just as little studied. Only the hydrogenation of alkyl-β-cyanethyl ethers [5] and of the di-(β-cyanethyl) ether [6] has been described in the literature.

Relative to the hydrogenation of di-(β-cyanethyl) ethers of glycols there are only very brief patent instructions [7] in the literature.

We carried out the cyanethylation of glycols and ethylene cyanhydrin in the presence of a 40% aqueous potassium hydroxide solution as had been described by Bruson [8]. The corresponding di-(β-cyanethyl) ether (I) was obtained in a yield of 96% by the cyanethylation of ethylene glycol. The di-(β-cyanethyl) ether (II) was obtained in a yield of 92% by the cyanethylation of 1,3-butylene glycol. We obtained the crystalline di-(β-cyanethyl) ether of 1,4-butylene glycol (III) which had not been described in the literature. Yield 90%.

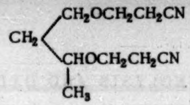
Acrylonitrile adds to diethylene glycol in the presence of a 40% aqueous solution of potassium hydroxide with the formation of di-(β-cyanethyl) ether (IV) in a yield of 97%.

The di-(β-cyanethyl) ether (V) was obtained in a yield of 92% by the addition of acrylonitrile to ethylene cyanhydrin.



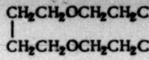
$$\begin{array}{l}CH_2OCH_2CH_2CN\\ |\\ CH_2OCH_2CH_2CN\end{array}$$

(I)



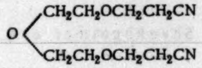
$$CH_2\begin{cases}CH_2OCH_2CH_2CN\\ CHOCH_2CH_2CN\\ \quad | \\ \quad CH_3\end{cases}$$

(II)



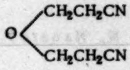
$$\begin{array}{l}CH_2CH_2OCH_2CH_2CN\\ |\\ CH_2CH_2OCH_2CH_2CN\end{array}$$

(III)



$$O\begin{cases}CH_2CH_2OCH_2CH_2CN\\ CH_2CH_2OCH_2CH_2CN\end{cases}$$

(IV)

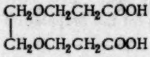
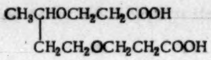
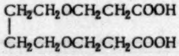
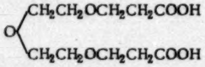
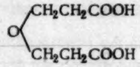


$$O\begin{cases}CH_2CH_2CN\\ CH_2CH_2CN\end{cases}$$

(V)

The hydrolysis of the di-(β-cyanethyl) ethers (I-V) was carried out by the method of Christian and Hixon [2] by heating with concentrated hydrochloric acid. The yields and the constants of the thereby-obtained dicarboxylic acids (VI-X) are indicated in Table 1.

TABLE 1

Formula		M.p. (in °)	Yield (in %)
(VI)	 $\begin{array}{l}CH_2OCH_2CH_2COOH\\ \mid\\ CH_2OCH_2CH_2COOH\end{array}$	65-66	92
(VII)	 $\begin{array}{l}CH_3CHOCH_2CH_2COOH\\ \quad\mid\\ \quad CH_2CH_2OCH_2CH_2COOH\end{array}$	Oil	90
(VIII)	 $\begin{array}{l}CH_2CH_2OCH_2CH_2COOH\\ \mid\\ CH_2CH_2OCH_2CH_2COOH\end{array}$	90	95
(IX)	 $O\begin{cases}CH_2CH_2OCH_2CH_2COOH\\ CH_2CH_2OCH_2CH_2COOH\end{cases}$	Oil	90
(X)	 $O\begin{cases}CH_2CH_2COOH\\ CH_2CH_2COOH\end{cases}$	60-61	97

The conversion of the di-(β-cyanethyl) ethers (I-V) into esters of the corresponding dicarboxylic acids (XI-XX) was accomplished via heating the nitriles with alcohols in the presence of concentrated sulfuric acid. In each case, both ethyl and methyl alcohols were used. The results of the experiments are set forth in Table 2.

We also accomplished the conversion of the di-(β-cyanethyl) ethers (I-V) into the diamines (XXI-XXV) via catalytic hydrogenation (over Raney nickel) in methyl alcohol saturated with dry ammonia (to suppress the formation of secondary amines). The hydrogenation proceeds rapidly at temperatures of 90-110° and an initial hydrogen pressure of 80-150 atm. The yields and constants of the diamines obtained are set forth in Table 3.

The diamines, dicarboxylic acids and their esters described in this paper can be employed to prepare new polyamide resins which contain oxygen heteroatoms in the chain and are distinguished by increased hydrophilic qualities.

EXPERIMENTAL

I. Reaction of Acrylonitrile with Ethylene Glycol

744 g (12 moles) of ethylene glycol and 75 g of a 40% aqueous solution of potassium hydroxide were placed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 1272 g (24 moles) of acrylonitrile was added over a period of 6 hours while the mixture was being energetically stirred and cooled with cold water. The temperature of the mixture should not rise above 30°. After the addition of all the acrylonitrile the mixture was stirred at room temperature for 4 hours and left overnight. On the next day, the alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off, and the filtrate was vacuum distilled. 1957 g of the di-(β-cyanethyl) ether of ethylene glycol (I) was obtained:

b.p. 160-169° at 2 mm; n_D^{20} 1.4495 [8].

The experiments described below which involved the cyanethylation of other glycols were carried out in the same way.

Hydrolysis of the Di-(β-cyanethyl) Ether of Ethylene Glycol

450 g (2.7 moles) of the di-(β-cyanethyl) ether of ethylene glycol (I) was placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. 1000 ml of concentrated hydrochloric acid was gradually added over a period of 1 hour while the mixture was being cooled and stirred. After the temperature of the mixture ceased to rise spontaneously, the stirring was continued for 3 hours at 70-80° and for 40 minutes at 95-98°. The reaction mass was cooled, the ammonium chloride which precipitated was filtered off and the water was distilled off from the filtrate in a vacuum. The residue was extracted with warm acetone, the extract

TABLE 2

Formula	Yield (in %)	B p. (in °) at a pressure (in mm)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
(XI) $\begin{array}{l}CH_2OCH_2CH_2COOCH_3\\ \vert\\ CH_2OCH_2CH_2COOCH_3\end{array}$	48	136 (4), m.p. 28.5-29°	–	–	–	–
(XII) $\begin{array}{l}CH_2OCH_2CH_2COOC_2H_5\\ \vert\\ CH_2OCH_2CH_2COOC_2H_5\end{array}$	68	135-137 (2.5)	1.4361	1.0654	64.31	64.21
(XIII) $\begin{array}{l}CH_3CHOCH_2CH_2COOCH_3\\ \quad\vert\\ \quad CH_2CH_2OCH_2CH_2COOCH_3\end{array}$	64.5	135-137 (3.5)	1.4368	1.0662	64.25	64.21
(XIV) $\begin{array}{l}CH_3CHOCH_2CH_2COOC_2H_5\\ \quad\vert\\ \quad CH_2CH_2OCH_2CH_2COOC_2H_5\end{array}$	71	141-143 (3)	1.4359	1.0292	73.65	73.45
(XV) $\begin{array}{l}CH_2CH_2OCH_2CH_2COOCH_3\\ \vert\\ CH_2CH_2OCH_2CH_2COOCH_3\end{array}$	64	146-148 (4)	1.4389	1.0691	64.41	64.21
(XVI) $\begin{array}{l}CH_2CH_2OCH_2CH_2COOC_2H_5\\ \vert\\ CH_2CH_2OCH_2CH_2COOC_2H_5\end{array}$	66	154-155 (4)	1.4380	1.0329	73.70	73.45
(XVII) $O\left\langle\begin{array}{l}CH_2CH_2OCH_2CH_2COOCH_3\\ CH_2CH_2OCH_2CH_2COOCH_3\end{array}\right.$	72	152-157 (3)	1.4429	1.1161	66.11	65.85
(XVIII) $O\left\langle\begin{array}{l}CH_2CH_2OCH_2CH_2COOC_2H_5\\ CH_2CH_2OCH_2CH_2COOC_2H_5\end{array}\right.$	72	167-169 (4)	1.4395	1.0726	75.11	75.09
(XIX) $O\left\langle\begin{array}{l}CH_2CH_2COOCH_3\\ CH_2CH_2COOCH_3\end{array}\right.$	54	94-96 (4)	1.4288	1.1127	44.01	44.09
(XX) $O\left\langle\begin{array}{l}CH_2CH_2COOC_2H_5\\ CH_2CH_2COOC_2H_5\end{array}\right.$	53	124-125 (7) 104-106 (4)	1.4274	1.0036	53.24	53.33

TABLE 3

Formula	Yield (in %)	B .p. (in °) at a pressure (in mm)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
(XXI) $\begin{array}{l}CH_2OCH_2CH_2CH_2NH_2\\ \vert\\ CH_2OCH_2CH_2CH_2NH_2\end{array}$	85	113-115 (4)	1.4638	0.9835	49.34	49.27
(XXII) $\begin{array}{l}CH_3-CHOCH_2CH_2CH_2NH_2\\ \quad\quad\vert\\ \quad\quad CH_2CH_2OCH_2CH_2CH_2NH_2\end{array}$	79	136-139 (6)	1.4621	0.9501	58.75	58.51
(XXIII) $\begin{array}{l}CH_2CH_2OCH_2CH_2CH_2NH_2\\ \vert\\ CH_2CH_2OCH_2CH_2CH_2NH_2\end{array}$	90	134-137 (3)	1.4619	0.9624	58.55	58.51
(XXIV) $O\left\langle\begin{array}{l}CH_2CH_2OCH_2CH_2CH_2NH_2\\ CH_2CH_2OCH_2CH_2CH_2NH_2\end{array}\right.$	81	146-148 (4)	1.4642	1.0107	60.08	60.15
(XXV) $O\left\langle\begin{array}{l}CH_2CH_2CH_2NH_2\\ CH_2CH_2CH_2NH_2\end{array}\right.$	76	72 (4)	1.4595	–	–	–

was filtered free of ammonium chloride, and the acetone was distilled off. The residue crystallized on standing. 507 g of the dicarboxylic acid (VI) was obtained with a m.p. of 65-66° (from a benzene-acetone mixture).

The hydrolysis of the other β-cyanethyl ethers was accomplished analogously (see below).

Hydrogenation of the Di-(β-cyanethyl) Ether of Ethylene Glycol

A 2.5 liter rotating autoclave was charged with 250 g (1.5 mole) of the di-(β-cyanethyl) ether of ethylene glycol, 600 ml of methyl alcohol saturated with dry ammonia, and 15 g of Raney nickel. The hydrogenation was carried out at 100-110° for 1 hour at an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (130 liters) was absorbed. 224 g of the di-(γ-aminopropyl) ether of ethylene glycol (XXI) was obtained:

b.p. 113-115° at 4 mm; n_D^{20} 1.4638; d_4^{20} 0.9835; MR_D 49.34; calculated 49.27.

3.538 mg sub.: 0.489 ml N_2 (20°, 754 mm). 5.903 mg sub.: 0.825 ml N_2 (22°, 745 mm). Found %: N 15.97, 15.86. $C_8H_{20}O_2N_2$. Calculated %: N 15.90.

The phenylcarbamide with a m.p. of 146-147° (from alcohol) was obtained from the diamine and phenylisocyanate.

3.230 mg sub.: 0.4167 ml N_2 (20°, 713 mm). 2.195 mg sub.: 0.2833 ml N_2 (20°, 713 mm). Found %: N 14.10, 14.11. $C_{15}H_{15}O_3N_3$. Calculated %: N 14.24.

Alcoholysis of the Di-(β-cyanethyl) Ether of Ethylene Glycol

a) 84 g (0.5 mole) of the di-(β-cyanethyl) ether of ethylene glycol, 250 ml of methyl alcohol and 150 g of concentrated sulfuric acid were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. The mixture was stirred for 12 hours at 80-84° (boiling point of the mixture). After this, the reaction mass was poured out into 500 ml of water, and the product was carefully extracted with ether. The ethereal extracts were combined, washed with a soda solution, dried with calcined sodium sulfate and vacuum distilled. 56.1 g of the dimethyl ester (XI) was obtained:

b.p. 136° at 4 mm; m.p. 28.5-29°.

8.115 mg sub.: 15.315 mg CO_2: 5.550 mg H_2O. 5.345 mg sub.: 10.108 mg CO_2: 3.730 mg H_2O. Found %: C 51.25, 51.61; H 7.61, 7.74. $C_{10}H_{18}O_6$. Calculated %: C 51.28; H 7.69.

The other experiments involving the alcoholysis of β-cyanethyl ethers were carried out in a similar manner.

b) A mixture of 16.8 g (0.1 mole of the di-(β-cyanethyl) ether of ethylene glycol, 50 ml of ethyl aclohol and 30 g of concentrated sulfuric acid were stirred at 94-98° (the mixture boiled) for 8 hours. The cooled reaction mass was poured out into 100 ml of water and treated as described above. 17.8 g of the diethyl ester (XII) was obtained:

b.p. 135-137° at 2.5 mm; n_D^{20} 1.4361; d_4^{20} 1.0654; MR_D 64.31; calculated 64.21.

5.639 mg sub.: 11.410 mg CO_2: 4.177 mg H_2O. 7.735 mg sub.: 15.610 mg CO_2: 5.785 mg H_2O. Found %: C 55.22, 55.07; H 8.28, 8.37. $C_{12}H_{22}O_6$. Calculated %: C 54.97; H 8.39.

II. Reaction of Acrylonitrile With 1,3-Butylene Glycol

90 g (1 mole) of 1,3-butylene glycol, 8 g of a 40% aqueous potassium hydroxide solution, and 106 g (2 moles) of acrylonitrile were taken in the reaction. 182 g of the di-(β-cyanethyl) ether of 1,3-butylene glycol (II) was obtained:

b.p. 155-165° at 0.3 mm; n_D^{20} 1.4467 [8].

Hydrogenation of the Di-(β-cyanethyl) Ether of 1,3-Butylene Glycol

19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,3-butylene glycol, 55 ml of methyl alcohol saturated with dry ammonia, and 2 g of Raney nickel were taken. The hydrogenation was carried out at 90-100° for 1 hour and 20 minutes at an initial hydrogen pressure of 95 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed. 16.2 g of the di-(γ-aminopropyl) ether of 1,3-butylene glycol (XXII) was obtained:

b.p. 136-139° at 6 mm; n_D^{20} 1.4621; d_4^{20} 0.9595; MR_D 58.76; calculated 58.51.

2.588 mg sub.: 0.300 ml N_2 (19°, 749 mm). 3.684 mg sub.: 0.435 ml N_2 (19°, 749 mm). Found %: N 13.36, 13.60. $C_{10}H_{24}O_2N_2$. Calculated %: N 13.72.

Hydrolysis of the Di-(β-cyanethyl) Ether of 1,3-Butylene Glycol

A mixture of 19.6 g (0.1 mole) of di-(β-cyanoethyl) ether of 1,3-butylene glycol in 50 ml of concentrated hydrochloric acid was stirred at 70-80° for one hour and at 95° for 45 minutes. 21.1 g of the dicarboxylic acid (VIII) was obtained, in the form of a yellow, noncrystallizing oil.

Alcoholysis of the Di-(β-cyanethyl) Ether of 1,3-Butylene Glycol

a) A mixture of 19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,3-butylene glycol, 55 ml of methyl alcohol and 30 g of concentrated sulfuric acid was stirred at 90-94° (the mixture boiled) for 6 hours. 16.9 g of the dimethyl ester (XIII) was obtained:

b.p. 135-137° at 3.5 mm; n_D^{20} 1.4368; d_4^{20} 1.0662; MR_D 64.25; calculated 64.21.

5.390 mg sub.: 10.880 mg CO_2: 4.076 mg H_2O. 4.982 mg sub.: 10.092 mg CO_2: 3.798 mg H_2O. Found %: C 55.09, 55.28; H 8.46, 8.53. $C_{12}H_{22}O_6$. Calculated %: C 54.97; H 8.39.

b) A mixture of 19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,3-butylene glycol, 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred at 95-97° for 6 hours (the mixture boiled). 20.6 g of the diethyl ester (XIV) was obtained:

b.p. 141-143° at 3 mm; n_D^{20} 1.4359; d_4^{20} 1.0292; MR_D 73.65; calculated 73.45 [3].

5.172 mg sub.: 10.995 mg CO_2: 4.095 mg H_2O. 6.651 mg sub.: 14.135 mg CO_2: 5.270 mg H_2O. Found %: C 58.02, 57.99; H 8.87, 8.87. $C_{14}H_{26}O_6$. Calculated %: C 57.93; H 8.97.

III. Reaction of Acrylonitrile With 1,4-Butylene Glycol

222 g (2.47 moles) of 1,4-butylene glycol, 22 g of a 40% aqueous solution of potassium hydroxide and 265 g (5 moles) of acrylonitrile were taken. 441 g of the di-(β-cyanethyl) ether of 1,4-butylene glycol (III) was obtained:

b.p. 183-191° at 3 mm; m.p. 38-39°; n_D^{20} 1.4516; d_4^{20} 1.0289; MR_D 51.39; calculated 51.30.

6.112 mg sub.: 13.741 mg CO_2: 4.473 mg H_2O. 5.896 mg sub.: 13.301 mg CO_2: 4.342 mg H_2O. Found %: C 61.35, 61.56; H 8.19, 8.24. $C_{10}H_{16}O_2N_2$. Calculated %: C 61.22; H 8.16.

Hydrogenation of the Di-(β-cyanethyl) Ether of 1,4-Butylene Glycol

199 g (1 mole) of the di(β-cyanethyl) ether of 1,4-butylene glycol, 600 ml of methyl alcohol, saturated with ammonia, and 12 g of Raney nickel were taken. The hydrogenation was carried out at 95-105° for 1 hour at an initial hydrogen pressure of 85 atm. The theoretical quantity of hydrogen (91 liters) was absorbed.

185 g of the di-(γ-aminopropyl) ether of 1,4-butylene glycol (XXIII) [7] was obtained:

b.p. 134-137° at 4 mm; n_D^{20} 1.4619; d_4^{20} 0.9624; MR_D 58.25; calculated 58.51.

12.310 mg sub.: 1.146 ml N_2 (22°, 757 mm). 4.821 mg sub.: 0.560 ml N_2 (22°, 757 mm). Found %: N 13.67, 13.39. $C_{10}H_{24}O_2N_2$. Calculated %: N 13.72.

Upon stirring equimolecular quantities of the diamine obtained and adipic acid in alcohol a crystalline salt with a m.p. of 114-115.5° was formed.

3.485 mg sub.: 0.1736 ml N_2 (18°, 730 mm). 3.270 mg sub.: 0.1588 ml N_2 (20°, 732 mm). Found %: N 5.58, 5.43. $C_{16}H_{34}O_{18}N_2$. Calculated %: N 5.64.

Hydrolysis of the Di-(β-cyanethyl) Ether of 1,4-Butylene Glycol

A mixture of 63 g (0.32 mole) of the di-(β-cyanethyl) ether of 1,4-butylene glycol and 130 ml of concentrated hydrochloric acid was stirred at 75-80° for 4 hours and at 100° for 15 minutes. 73.5 g of the dicarboxylic acid (VIII) with a m.p. of 90° (from benzene) was obtained.

6.350 mg sub.: 11.920 mg CO_2: 4.405 mg H_2O. 6.442 mg sub.: 12.070 mg CO_2: 4.370 mg H_2O. Found %: C 51.23, 51.13; H 7.76, 7.59. $C_{10}H_{18}O_6$. Calculated %: C 51.28; H 7.69.

Alcoholysis of the Di-(β-cyanethyl) Ether of 1,4-Butylene Glycol

a) A mixture of 19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,4-butylene glycol, 50 ml of methyl alcohol and 30 g of concentrated sulfuric acid was stirred at 82-85° (the mixture boiled) for 10 hours. 16.8 g of the dimethyl ester (XV) was obtained; it consisted of a colorless liquid with a characteristic odor:

b.p. 146-148° at 4 mm; n_D^{20} 1.4389; d_4^{20} 1.0691; MR_D 64.41; calculated 64.21.

5.317 mg sub.: 10.780 mg CO_2: 4.100 mg H_2O. 8.334 mg sub.: 16.794 mg CO_2: 6.340 mg H_2O. Found %: C 55.32, 55.00; H 8.63, 8.52. $C_{12}H_{22}O_6$. Calculated %: C 54.97; H 8.39.

b) A mixture of 120 g (0.6 mole) of the di-(β-cyanethyl) ether of 1,4-butylene glycol, 300 ml of ethyl alcohol and 150 g of concentrated sulfuric acid was stirred at 93-95° (the mixture boiled) for 6 hours. 117 g of the diethyl ester (XVI) was obtained:

b.p. 154-155° at 4 mm; n_D^{20} 1.4380; d_4^{20} 1.0329; MR_D 73.70; calculated MR_D 73.45.

4.582 mg sub.: 9.791 mg CO_2: 3.695 mg H_2O. 5.051 mg sub.: 10.752 mg CO_2: 4.075 mg H_2O. Found %: C 58.37, 58.08; H 9.02, 9.03. $C_{14}H_{26}O_6$. Calculated %: C 57.93; H 8.97.

IV. Reaction of Acrylonitrile With Diethylene Glycol

115 g (1.1 moles) of diethylene glycol, 10 g of a 40% aqueous solution of potassium hydroxide and 115 g (2.2 moles) of acrylonitrile were taken. 224.5 g of the di-(β-cyanethyl) ether of diethylene glycol (IV) was obtained:

b.p. 185-189° at 0.5 mm; n_D^{20} 1.4530 [8].

Hydrogenation of the Di-(β-cyanethyl) Ether of Diethylene Glycol

21.2 g (0.1 mole) of the di-(β-cyanethyl) ether of diethylene glycol, 55 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. Hydrogenation was carried out at 100-110° for 1 hour 20 minutes at an initial hydrogen pressure of 80 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed. 18 g of the di-(γ-aminopropyl) ether of diethylene glycol (XXIII) was obtained:

b.p. 146-148° at 4 mm; n_D^{20} 1.4642; d_4^{20} 1.0107; MR_D 60.08; calculated 60.15.

8.640 mg sub.: 1.008 ml N_2 (21°, 745 mm). 9.905 mg sub.: 1.123 ml N_2 (20°, 750 mm). Found %: N 13.30, 13.04. $C_{10}H_{24}O_3N_2$. Calculated %: N 12.72.

The corresponding phenylcarbamide with a m.p. of 100-102° (from alcohol) was prepared by the action of phenylisocyanate.

2.970 mg sub.: 0.3254 ml N_2 (19°, 730 mm). 3.335 mg sub.: 0.3646 ml N_2 (20°, 733 mm). Found %: N 12.30, 12.30. $C_{17}H_{29}O_7N_3$. Calculated %: N 12.39.

Hydrolysis of the Di-(β-cyanethyl) Ether of Diethylene Glycol

A mixture of 29 g (0.135 mole) of the di-(β-cyanethyl) ether of diethylene glycol and 60 ml of concentrated hydrochloric acid was stirred at 70° for 4 hours and at 95° for 20 minutes. 30.8 g of the dicarboxylic acid (IX) was obtained in the form of a light yellow oil, which did not crystallize [2].

Alcoholysis of the Di-(β-cyanethyl) Ether of Diethylene Glycol

a) A mixture of 21.2 g (0.1 mole) of the di-(β-cyanethyl) ether of diethylene glycol, 50 ml of methyl alcohol and 25 g of concentrated sulfuric acid was stirred at 82-86° (the mixture boiled) for 10 hours. 20.1 g of the dimethyl ester (XVII) was obtained:

b.p. 155-157° at 3 mm; n_D^{20} 1.4429; d_4^{20} 1.1161; MR_D 66.11; calculated 65.85.

5.185 mg sub.: 9.830 mg CO_2: 3.690 mg H_2O. 4.968 mg sub.: 9.430 mg CO_2: 3.492 mg H_2O. Found %: C 51.86, 51.80; H 7.96, 7.87. $C_{12}H_{22}O_7$. Calculated %: C 52.17; H 7.97.

b) A mixture of 21.2 g (0.1 mole) of the di-(β-cyanethyl) ether of diethylene glycol, 60 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred at 96-98° (the mixture boiled) for 6 hours. 22.1 g of the diethyl ester (XVIII) was obtained:

b.p. 167-169° at 4 mm; n_D^{20} 1.4395; d_4^{20} 1.0726; MR_D 75.11; calculated 75.09.

9.30 mg sub.: 18.80 mg CO_2: 7.23 mg H_2O. 8.88 mg sub.: 17.88 mg CO_2: 6.89 mg H_2O. Found %: C 55.17, 54.97; H 8.69, 8.63. $C_{14}H_{26}O_7$. Calculated %: C 54.90; H 8.49.

V. Reaction of Acrylonitrile With Ethylene Cyanhydrin

915 g (12.9 moles) of ethylene cyanhydrin, 65 g of a 40% aqueous solution of potassium hydroxide and 684 g (12.9 moles) of acrylonitrile were taken. 1476 g of the di-(β-cyanethyl) ether (V) was obtained:

b.p. 167-174° at 5 mm; n_D^{20} 1.4418 [8].

Hydrogenation of the Di-(β-cyanethyl) Ether

12.5 g of the di-(β-cyanethyl) ether, 50 ml of methyl alcohol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was carried out at 100-115° for 30 minutes at an initial hydrogen pressure of 140 atm. The theoretical quantity of hydrogen (9.0 liters) was absorbed. 10.2 g of the di-(γ-aminopropyl) ether (XXV) was obtained:

b.p. 72° at 4 mm; n_D^{20} 1.4595 [6].

Hydrolysis of the Di-(β-cyanethyl) Ether

1250 ml of concentrated hydrochloric acid was added to 400 g (3.2 moles) of the di-(β-cyanethyl) ether while it was being cooled with ice water and stirred. After the temperature of the mixture ceased to rise spontaneously, the stirring was continued for 4 hours at 70-80° and for 30 minutes at 95-98°. 507 g of the β,β'-di-(carboxyethyl) ether (X) was obtained:

m.p. 60.5-61.5° (from ether) [2].

Alcoholysis of the Di-(β-cyanethyl) Ether

a) A mixture of 250 g (2 moles) of the di-(β-cyanethyl) ether, 1000 ml of methyl alcohol and 500 g of concentrated sulfuric acid was stirred for 10 hours at 80-85° (the mixture boiled). 208.7 g of the di-(β-carbomethoxyethyl) ester (XIX) was obtained:

b.p. 94-96° at 4 mm; n_D^{20} 1.4288; d_4^{20} 1.1127; MR_D 44.01; calculated 44.09.

4.925 mg sub.: 9.198 mg CO_2: 3.290 mg H_2O. 6.556 mg sub.: 12.163 mg CO_2: 4.437 mg H_2O. Found %: C 50.96, 50.63; H 7.47, 7.58. $C_8H_{14}O_5$. Calculated %: C 50.52; H 7.37.

b) A mixture of 62 g (0.5 mole) of the di-(β-cyanethyl) ether, 250 ml of ethyl alcohol and 150 g of concentrated sulfuric acid was stirred for 8 hours at 90-98° (the mixture boiled). 58 g of the di-(β-carboethoxyethyl) ester (XX) [9] was obtained:

b.p. 124-125° at 7 mm; 104-106° at 4 mm; n_D^{20} 1.4274; d_4^{20} 1.0522; MR_D 53.24; calculated 43.33.

12.26 mg sub.: 24.58 mg CO_2: 9.23 mg H_2O. 9.38 mg sub.: 18.87 mg CO_2: 6.89 mg H_2O. Found %: C 54.71, 54.85; H 8.42, 8.22. $C_{10}H_{18}O_5$. Calculated %: C 55.05; H 8.26.

VI. Polycondensation of the Salt of the Di-(γ-aminopropyl) Ether of 1,4-Butylene Glycol and Adipic Acid (Salt AB)

The polycondensation was carried out in a test tube supplied with a stopper with a tube for passing in nitrogen and one for eliminating the water formed. The nitrogen was freed from oxygen by passage through pyrogallol, dried with sulfuric acid and calcium chloride; after this the nitrogen was passed over copper heated to 470° and, finally, over phosphoric anhydride.

6 g of the salt was placed in the test tube and was heated to the melting point and after fusion, a constant stream of nitrogen was passed in. In the course of 5 hours, the temperature of the bath was raised from 160 to 270°. The heating was continued for 40 minutes at 270°. Water was evolved in the course of the first three hours. On cooling, the melt solidified into a light, creamy mass. It could be cut with a knife, clung to the glass, and was washed off with water.

A portion of the product obtained was heated in a vacuum at 220-240° for 2 hours. The product became brown colored and harder.

VII. Joint Polycondensation of Salt AB With the Salt of Adipic Acid and Hexamethylene Diamine (Salt AH)

In a ratio of 1:3. Taken: 11.25 g of salt AH and 3.75 g of salt AB. The mixture was heated for 1 hour to 250° and then for 4 hours at 250-260° in a vacuum. A light brown solid product with a cornulate cross section was obtained.

In ratio of 1:1. a) Taken: 7.5 g of salt AH and 7.5 g of salt AB. The mixture was heated for 1 hour to 250° and then for 4 hours at 250-260° in a vacuum. A light cream elastic polymer which could be cut with a knife was obtained. b) Taken: 3 g of salt AH and 3 g of salt AB. In the course of 3 hours, the temperature was raised from 160 to 240° and then the mixture was heated for 1.5 hours at 240-250°. A white solid polymer with a comulate cross section was obtained.

In a ratio of 3:1. Taken: 3.75 g of salt AH and 11.25 g of salt AB. The mixture was heated in a vacuum at 250-260° for 2 hours. A dark grey polymer which could be cut with a knife only with difficulty was obtained.

SUMMARY

The hydrogenation, hydrolysis and alcoholysis of β-cyanethyl ethers of ethylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, diethylene glycol and ethylene cyanhydrin were studied. The corresponding diamines, dicarboxylic acids and their esters, containing oxygen heteroatoms in the chain and able to be used for the preparation of new polyamides with increased hydrophilic properties, were prepared in high yields.

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INVESTIGATION OF THE NATURE OF THE CATALYSTS USED FOR ISOMERIZATION AND POLYMERIZATION OF HYDROCARBONS

I. CONCERNING THE CAUSE OF THE CATALYTIC ACTIVITY OF TITANIC ACID

G. A. Rudakov and Z. S. Khomenko

In connection with the catalytic isomerization and polymerization of hydrocarbons in the presence of clay, which was initiated by L. G. Gurvich [1], the chemical transformations of the separate compounds, the mechanism of the processes which proceed, and also the nature of the catalysts causing the indicated reactions have been studied in recent years.

On the basis of the results obtained during the study of the catalytic conversions of pinene on active clays and of the close congruence of these conversions with the conversions of pinene under the influence of certain acids, and also keeping in mind the work of V. I. Vernadsky [2] and of P. A. Zemyatchensky [3], which have made it possible to chemically characterize the clay as a mixture of aluminum silicic acids, V. E. Tishchenko and G. A. Rudakov [4] came to the conclusion that the catalytic properties of active clays are due to the acid nature of the aluminum silicates of which they are formed. This explanation of the activity of aluminum silicate catalysts, published as early as 1933, is shared by the majority of chemists at the present time.

If the acid nature of the clays and of synthetic aluminum silicates used along with the clays as catalysts is generally accepted at the present time, the question of the cause of the acid nature of the said aluminum silicates, which fundamentally differ in their properties from silicic anhydride and aluminum hydroxide, remains in dispute.

Certain investigators [5, 6] assume that the acid properties of aluminum silicate catalysts are due to the presence on them of surface sorbed mineral acids and basic salts of aluminum. These views are supported by certain properties of carefully dialyzed gels of aluminum silicates, including the absence of electrical conductivity and the weak catalytic activity, but are inconsistent with the possibility of obtaining active aluminum silicate catalysts by aqueous hydrolysis of mixtures of the ethyl ester of silicic anhydride and aluminum isopropylate [7].

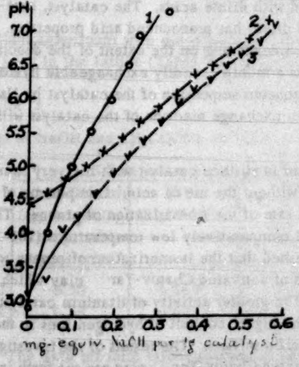

Fig. 1. Potentiometric titration curves of titanium catalysts with 0.1 N NaOH. 1) Catalyst ED-2; 2) catalyst 1-52; 3) catalyst 16-52.

Ross and Hendriks [8], Thomas [7] and other investigators explained the presence of acid properties in aluminum silicates by the peculiarities of their structure, which fundamentally differentiate them from the silica which enters into their composition. In agreement with the representation of these authors, the Si atom with a valence of 4 and a coordination number 4, which is substituted in the aluminum silicate lattice for an Al atom with a valence of 3 and a coordination number 4, leads to the phenomenon of a charge in the lattice which is compensated for by the hydrogen atoms which enter into it and subsequently are capable of ready exchange.

The views of Ross and Hendriks and also of Thomas on the cause of the acid properties of aluminum silicates encounter a number of objections. These objections have been made known by K. G. Mieserov [9] in his review which recently appeared.

He gives his explanation of the acid nature of aluminum silicates, which consists of the assumption that acidic aluminum silicates have an exchangeable Al ion which replaces the hydrogen in the SiOH groups and is capable of adding water with the formation of the complex $\left[\begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{AlOH} \right]^{-} H^{+}$, with a mobile hydrogen ion.

It seems that the points of view set forth on the cause of the activity of aluminum silicate catalysts are at fault in attempting to give a single explanation of the formation of the hydrogen ion which is capable of ready exchange in such complex substances as aluminum silicates. It should be noted also at the same time that the majority of investigators ignore other analogously acting catalysts, which is incorrect, since the results of the study of catalysts which act similarly to aluminum silicate but have a simpler composition, may possibly turn out to be useful for the understanding of the causes of the activity of aluminum silicate catalysts.

Of the catalysts with simpler compositions than aluminum silicate catalysts, titanic acid, to which the present work has been devoted, merits attention. Titanic acid has been employed for the isomerization of pinene into camphene and monocyclic terpenes [10] and of Δ^3-carene into Δ^4-carene [11].

TABLE 1

Comparative Characteristics of Catalysts

Catalyst No.	Loss from roasting (in %)	Na_2O (in %)	pH	NaOH consumption: To bring the pH of a suspension of 1 g of the catalyst in water to 7 (in mg equiv.)	NaOH consumption: To neutralize the CH_3COOH evolved as a result of the exchange reaction of 1 g of catalyst with CH_3COONa (in mg equiv.)	Surface (in m^2/g)	Activity with respect to pinene: Temperature (in °)	Activity with respect to pinene: % of catalyst	Activity with respect to pinene: Duration (in hours)
Titanium catalyst obtained by the decomposition of sodium titanate with dilute acid									
2-51	8.7	4.38	6.1	0.105	–	–	135	1	8
1-52	7.9	2.62	4.54	0.530	0.565	180	135 160	1 0.2	1 0.75
16-52	9.5	0.23	3.06	0.560	0.655	132	160	0.2	0.75
Titanium catalyst obtained by electrodialysis of sodium titanate									
ED-2	–	0.49	2.9	0.300	–	114	135	2	2
Activated Chasov-Yar clay									
8-52	–	–	2.67	0.183	–	80	125 160	1 0.25	3 1-15

The titanic acid used as a catalyst is ordinarily obtained by the hydration of titanium dioxide by aqueous solutions of NaOH, with subsequent decomposition of the titanate formed with dilute acids. The catalyst, carefully washed free from the acid taken for decomposing the titanate and dried, has pronounced acid properties. The pH value of aqueous suspensions of the catalyst lies between 3 and 6, depending on the extent of the decomposition of the titanate. The catalyst, similarly to aluminum silicate, has a mobile, readily exchangeable hydrogen ion, which can be determined via direct potentiometric titration of an aqueous suspension of the catalyst by NaOH solution (Fig. 1) or via titration with CH_3COOH evolved as a result of an exchange reaction of the catalyst with 1 N CH_3COONa solution [12].

The acid properties of titanium catalyst are not due to sorbed acid in it, since catalyst with the very same properties was obtained by the electrodialysis of sodium titanate, i.e., without the use of acid. Comparison of the activity of various samples of catalyst was carried out according to the rate of the isomerization of pinene. This reaction is very convenient for the indicated object, since it proceeds at comparatively low temperatures (130-160°), due to which it is not complicated by thermal processes. It was established that the isomerization of pinene with titanic acid proceeds even faster than with an equal quantity by weight of activated Chasov-Yar clay which has been repeatedly used as a catalyst for the indicated reaction [4, 13]. The greater activity of titanium catalyst than that of activated Chasov-Yar clay, appears to be a consequence of the higher content of hydrogen ions in the titanium catalyst which are capable of exchange, and of its greater specific surface. The results of the investigation of titanium catalysts and the results of their comparison with activated Chasov-Yar clay are set forth in Table 1.

The presence of strongly expressed acid properties and considerable catalytic activity approximates the behavior of titanic acid to that of aluminum silicate catalysts, but not to its closest analogs – silicic acid and aluminum hydroxide, which have very weakly expressed acid properties and little catalytic activity [7]. It is sufficient to state that for the complete isomerization of pinene at 155-160° in a period of 2 hours it is necessary to introduce 2% of silica gel as catalyst, i.e., 30 times more than of titanium catalyst or of activated Chasov-Yar clay.

The cause of so pronounced acid properties of titanic acid can be explained by using the rule of electrostatic valency. In all forms of titanium dioxide, tetravalent titanium has a coordination number of 6, in accordance with which the strength of the titanium-oxygen bond in the lattice is equal to $^2/_3$. Since the coordination number of oxygen in lattices of titanium dioxide is equal to 3, the lattice has a neutral charge. In the case of hydration of the separate oxygen-titanium bonds, hydroxyl groups are formed. Since the strength of the oxygen-hydrogen bond is equal to 1, while the strength of the bond of the oxygen of the hydroxyl group with a titanium ion is equal to $^2/_3$, $^1/_3$ of the valence of oxygen remains unsaturated. As a result, in the titanium dioxide lattice hydrated from the surface, a negative charge appears which must be compensated for by hydrogen ions which enter into the lattice (one per each three hydroxyl groups). The cation which enters into the lattice must proceed from the same hydrating reagent, since during the hydration of titanium dioxide the $\mathrm{Ti{-}\underset{\underset{Ti}{|}}{O}{-}Ti}$ groups which are hydrated require the addition of one cation and two hydroxyl groups; as a result the second cation of the hydrating reagent enters into the lattice to neutralize its charge.

The considerations set forth are confirmed by the results obtained during the action of dilute NaOH solutions on titanium catalyst. During the addition to titanium catalyst of excess dilute NaOH solution a very rapid reaction proceeds, as a result of which 4 times more NaOH enters into the reaction than during the potentiometric titration to pH 7 of an aqueous suspension of the catalyst. Since an almost instantaneous hydration of the titanium–oxygen bond with an 0.01 N NaOH solution appears hardly probable, the different consumption of NaOH in the reaction with the catalyst in neutral and alkaline media must be explained otherwise. At pH values less than or equal to 7, an exchange of hydrogen ions for sodium ions proceeds, which neutralizes the lattice charge of the catalyst, which is also confirmed by the data obtained by the action on the catalyst of CH_3COONa solutions; in an alkaline medium there takes place, moreover, a reaction with the hydroxyl groups of the catalyst. The relation between the consumption of NaOH in both cases is in excellent agreement with the requirement of the presence of one hydrogen ion for three hydroxyl groups joined to the Ti ion in the lattice (Table 2 and Fig. 2).

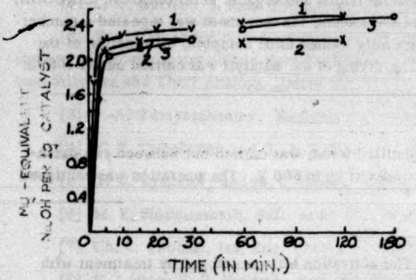

Fig. 2. Rate of absorption of NaOH from aqueous solutions by titanium catalyst. 1) Catalyst 1-52 + 0.1 N NaOH; 2) catalyst 1-52 + 0.01 N NaOH; 3) catalyst 16-52 + 0.01 N NaOH.

TABLE 2

Action of NaOH and CH_3COONa on Titanium Catalyst

Catalyst No.	Substances which react with 1 g of catalyst (in mg-equiv.)				A:D	B:D
	(A) NaOH during the raising of the pH of the suspension to 7	(B) CH_3COONa	NaOH in alkaline medium			
			(C) Total	(D) After raising the pH of the suspension to 7		
1-52	0.53	0.565	2.28	1.75	1:3.3	1:3.1
16-52	0.56	0.655	2.56	2.00	1:3.7	1:3

The data set forth circumstantially confirm the views of Thomas and other investigators concerning the cause of the catalytic activity of aluminum silicate catalysts. However, it is entirely probable that the activity of aluminum silicate catalysts can be evoked not only by the causes set forth, but also by others.

EXPERIMENTAL

1. Preparation of Sodium Titanate

The sodium titanate which served as the starting material for the preparation of the catalyst, was prepared in accordance with the data in the literature [10]: titanium dioxide was treated with a strong solution of sodium hydroxide while being heated under pressure, and the reaction product was washed with water until the NaOH was eliminated from it.

Metatitanic acid obtained by aqueous hydrolysis of $Ti(SO_4)_2$ containing 6-7% sulfuric acid, probably bound on account of incomplete hydrolysis, was also used as a starting material. The treatment of the metatitanic acid with NaOH solution was carried out at atmospheric pressure and led to complete splitting off of H_2SO_4.

The sodium titanate obtained in both cases was identical. When dried at 105°, it consisted of a white powder and contained about 12% Na calculated on Na_2O. The loss from roasting amounted to around 8%; the pH of an aqueous suspension was 7-7.2. The quantity of sodium in the preparation showed that it consisted not of the sodium salt of titanic acid, but only of titanium dioxide hydrated from the surface.

2. Decomposition of the Sodium Titanate by Acids

The decomposition of the sodium titanate was also carried out in accordance with literature data [10], with weak aqueous solutions of acids (from 0.1 to 1%). Both mineral acids $(HCl)_2$ and organic acids ($HCOOH$, CH_3COOH) were used. If there was any problem of complete elimination of the sodium, the treatment was repeated a number of times. After decomposition with acid, the precipitate was carefully washed until complete elimination of the excess acid introduced, and was filtered on a Büchner funnel. The drying of the catalyst was carried out at 105° in a desiccator or under a vacuum at 100°.

3. Electrodialysis of the Sodium Titanate

The electrodialysis of the sodium titanate, shaken up in distilled water, was carried out between two parchment membranes at a potential difference of the platinum electrodes of up to 600 V. The operation was continued for around two months.

4. Activated Chasov Yar Clays

Chasov-Yars clay No. 5 was used for the experiments. The activation was carried out by treatment with hydrochloric acid under the usual conditions [4].

5. Determination of pH and Potentiometric Titration of the Catalysts

The determination of pH and the potentiometric titration were carried out with quinhydrone electrodes. 2.5 g samples of the catalysts were used; before the titration they were shaken up in 12.5 ml of water. During the titration, after the addition of each portion of NaOH solution, we waited for about 10 minutes in order that the reaction might be concluded, although equilibrium was rapidly established. Thus, for example, the pH of a suspension of titanium catalyst, neutralized with NaOH to a pH of 6.97, was 6.76 after 24 hours.

6. Determination of Sodium in the Titanium Catalyst

A portion of the catalyst, equal to 0.2-0.3 g was treated 5 times in succession with 15 ml of a 4% boiling solution of HCl. The duration of each treatment amounted to 2-3 minutes. After five treatments the precipitate was washed on a filter with a 4% solution of HCl. The partially dissolved titanium salt was precipitated from the filtrate with ammonia and the filtrate concentrated, after which the sodium was precipitated in the form of sodium zinc uranyl acetate, or after elimination of the ammonium salts was determined in the form of NaCl.

7. Determination of the Specific Surfaces of the Catalysts

The determination of the specific surfaces of the catalysts was made on the basis of the amount of methylene blue adsorbed by the catalysts. A sample of about 0.1 g of the catalyst was added to 60 ml of a 0.15% solution of the dye and shaken on a machine for 2 hours. After about 12 hours, the catalyst was precipitated on the centrifuge while the solution was analyzed colorimetrically after 100 fold dilution. The calculation of the surface was based on the fact that 1 mg of methylene blue is adsorbed by 1 square meter of catalyst surface [14].

8. Action of Excess NaOH on the Titanium Catalyst

200 ml of an 0.01 or 0.1 N NaOH solution was added to a 0.5 or 5 g sample of the catalyst placed in a 200 ml measuring flask. The flask was shaken periodically and samples were taken from it with a pipet, which were titrated after rapid filtration.

SUMMARY

1. As a catalyst of the isomerization of pinene, titanic acid has no less activity than aluminum silicate catalyst.

2. The activity of titanium catalyst is due to the presence in it of hydrogen ions which are capable of ready exchange, or in other words, to its acid properties.

3. The preparation of active titanic acid via electrodialysis of its sodium salt demonstrates that the activity of titanium catalyst is due to the properties of titanic acid, and not to the presence of adsorbed acids or basic salts.

4. The high catalytic activity and pronounced acidity approximates titanic acid in its properties to aluminum silicates, but not to its closest analogs – silicic acid and aluminum hydroxide. An explanation of this was given, based on the specific peculiarities of the lattice structure of titanium dioxide, which results in the necessity of one hydrogen entering into its composition for each three hydroxyl groups which are formed during its surface hydration.

5. The study of the action of NaOH solutions on titanium catalyst confirmed the development of the representation of the cause of the catalytic activity of titanic acid.

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SUMMARY

1. As a catalyst of the isomerization of pinene oxide [illegible]

2. The activity [illegible]

3. The preparation of [illegible]

4. The high [illegible]

5. The study of the action of NaOH [illegible] of the causes of the catalytic activity of [illegible]

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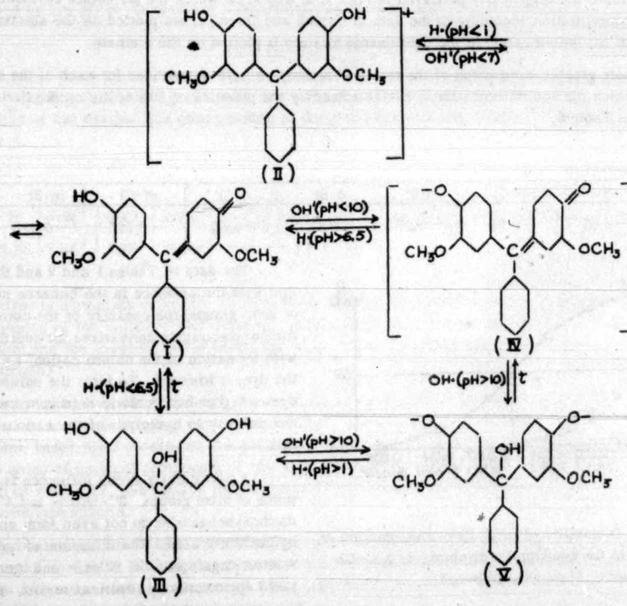
INVESTIGATION IN THE FIELD OF HYDROXYFUCHSONE

XIX [1]. INFLUENCE OF THE NITRO GROUP AND HALOGENS ON THE INDICATOR PROPERTIES OF DERIVATIVES OF 3,3'-DIMETHOXYBENZAURIN

I. S. Ioffe and B. G. Belenky

In one of the preceding communications [2], the indicator properties of certain hydroxyfuchsone dyes of the aurin and benzaurin groups were considered by one of us. The most interesting as regards indicator properties was 3,3'-dimethoxybenzaurin (I). In the non-ionized state, it forms yellow solutions. In a mineral acid medium, it is dissolved with an intense violet coloration, the carrier of which appears to be the onium cation (II). The stability of the latter depends on the hydrogen ion concentration. In the presence of reduced acidity of the medium, the intensity of the coloration gradually falls and at a pH greater than 1 the solution is decolorized. We initially assumed that this was associated with cleavage of a proton and with regeneration of the initial dye. However, newer observations described below, show that the decolorization of the solution is due primarily to hydration of the dye and formation of the carbinol compound (III).

In a weakly alkaline medium 3,3'-dimethoxybenzaurin is dissolved with a bright blue color, the carrier of which appears to be the anion of the dye (IV). Upon increasing the hydroxyl ion concentration, the solution gradually is decolorized as a result of the addition of hydroxyl groups and formation of the still colorless anion of the carbinol compound (V). On heating, the decolorized solution again exhibits the blue color of the dye anion (IV). Upon acidification of the colorless solution with acetic acid, the carbinol compound (V) precipitates. Upon acidification



of the alkaline solutions with hydrochloric acid, and equally during the treatment of the carbinol compound (III) with hydrochloric acid, the onium cation (II) is formed. All the conversions described are incorporated in the scheme (see above).

In the development of this investigation, we studied the indicator properties of the 3,3'-dimethoxybenzaurin derivatives containing nitro groups and halogens in various positions of the benzene nucleus, which were described in the preceding communications [1, 3].

To study the influence of nitro groups and halogens on the conditions of formation of the onium cations of type (II) and on their stability to hydrolysis, we added approximately 0.5 ml of 0.00025 N alcoholic solution of the base of each dye to 9.5 ml of hydrochloric acid, subsequently lowering the concentration from 10 to 0.1 N. The intensity of the violet coloration which appeared, which characterizes the quantity of onium cation which was formed, we colorimetrically compared with the intensity of the coloration of a standard solution of a sample of the same weight of the corresponding dye in 10 N hydrochloric acid, in which the dye is entirely converted into the onium cation. The results obtained are set forth in Table 1.

TABLE 1

Dye		Normality of HCl							
		10	5	3	2	1	0.5	0.2	0.1
3,3'-Dimethoxybenzaurin		100	100	92	74	33	12.5	2	0
2''-Br-	3,3'-Dimethoxybenzaurin	100	96	73	49	13	7	0	0
2''-Cl-		100	96	68	43	17	6	0	0
3''-Br-		100	95	58.5	24.5	5	0	0	0
3''-Cl-		100	96	59.5	25.5	5	1	0	0
4''-Br-		100	100	82	54	16	4	0	0
4''-Cl-		100	100	84	56	18	5	0	0
3''-NO_2-		100	79.5	22	6	0	0	0	0
4''-NO_2-		100	76.5	17.5	5	0	0	0	0

These results are graphically portrayed in Figs. 1, 2, and 3, on which the pH values calculated from the hydrochloric acid concentration according to the data of Harned and Owen [4] are plotted on the abscissa, while the percent content of the onium cation in the equilibrium mixture is plotted on the ordinate.

For a more graphic comparison of the results obtained, we have determined for each of the dyes studied the pH value at which the equilibrium state is characterized by the presence of 50% of the onium cation. These data are set forth in Table 2.

TABLE 2

Substituent	H	p-Cl	p-Br	o-Br	o-Cl	m-Cl	m-Br	m-NO_2	p-NO_2
pH	−0.06	−0.24	−0.27	−0.31	−0.48	−0.525	−0.535	−0.86	−0.905

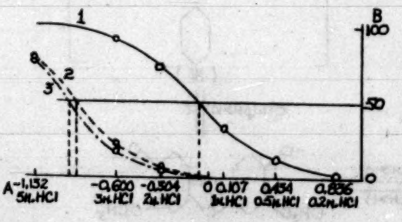


Fig. 1. A) pH (normality of HCl); B) percent content of onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO_2; 3) p-NO_2.

The data of Tables 1 and 2 and the figures show that with the presence in the benzene nucleus of halogens or nitro groups, the capacity of the corresponding 3,3'-dimethoxybenzaurin derivatives for addition of a proton with formation of the onium cation, i.e., the basicity of the dye, is lowered. To form the onium cations of these dyes a higher hydrochloric acid concentration is necessary; the stability to hydrolysis of the cations which are formed falls.

A particularly strong influence is exerted by the presence of nitro groups. 3''-Nitro- and 4''-nitro-3,3'-dimethoxybenzaurins do not even form onium cations in 1 N hydrochloric acid. The influence of halogens is exerted to a lesser degree, and the chloro- and bromo- derivatives yield approximately identical results. In the case of halogen derivatives the position of the halogen is important. The greatest lowering of the basicity of the dye is caused by the presence of halogen in the m-position to the central carbon atom.

TABLE 3

pH	Substituent								
	H	o-Br	o-Cl	m-Br	m-Cl	p-Br	p-Cl	m-NO_2	p-NO_2
7.79	35	46	45	41	40.5	40	40	49	54.5
7.93	43	54	53	49.5	48.5	47.5	48	57.5	62.5
8.09	52	63.5	62.5	58	57.5	56.5	57	66	70.5

During the study of the influence of the nitro group and halogens on the indicator properties of 3,3'-dimethoxybenzaurin derivatives in the weakly alkaline zone, we used as standard a solution of the dye in a borate buffer with a pH equal to 9.5. In such a solution, the dye is almost wholly dissociated with the formation of the color specified for the anion type (IV); the solutions obtained were stable during storage and did not change the intensity of the color. With such a standard solution each dye was compared as regards intensity of color of the solution with the same dye with a pH in the range 7.8-8.1, and the optical density was measured for this with the aid of an SF-11 spectrophotometer. We calculated the degree of acid dissociation of the dye under study by the pH differences according to the results obtained. The results obtained are set forth in Table 3.

These data are graphically illustrated in Fig. 4, where the pH values are plotted on the abscissa and the values of the logarithm of the ratio of the concentration of the dye [A] to the concentration of non-dissociated dye [AN] are plotted on the ordinate.

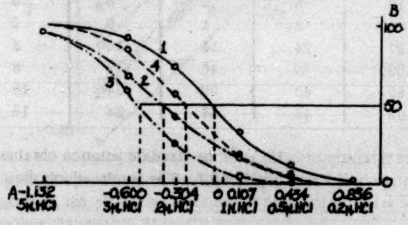


Fig. 2. A) pH (normality of HCl); B) percent content of onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl

It is evident from the figure that the points found for all the dyes are distributed on parallel straight lines with inclinations, the tangent of the angle of which is equal to 1. This shows that the dependence of the ionization of all the dyes studied on the pH of the medium is determined by the equation

$$pK = pH - \log \frac{[A]}{[AN]}.$$

Therefore, using Fig. 4, one can graphically determine the pK value, since it corresponds for each dye to the point of intersection of the straight line corresponding to the given dye with the abscissa. The pK values found are set forth in Table 4.

TABLE 4

Substituent	H	o-Br	o-Cl	m-Br	m-Cl	p-Br	p-Cl	m-NO_2	p-NO_2
pK	8.06	7.86	7.88	7.96	7.95	7.97	7.98	7.80	7.71

The data of Tables 3 and 4 and of Fig. 4 show that the presence of halogen in the benzene nucleus and particularly of the nitro group, strengthens the capacity of the 3,3'-dimethoxybenzaurin derivatives to dissociate in weakly alkaline medium with the formation of the colored anion of the dye; this influences the lowering of the values of pK. However, such a lowering is comparatively small. It amounts to 0.3 for the nitro compounds, and the lowering varies within the range 0.2-0.1 for the halogen derivatives, depending on the position of the halogen.

The complex of reactions which characterize the indicator properties of the hydroxyfuchsone dyes includes the conversion of the dye into the corresponding carbinol derivatives. Such conversions have up to now, only been observed in alkaline medium; under these conditions, the coloring of the dye anion, which adds a hydroxyl ion, is converted into the colorless anion of carbinol compounds of type (V). Such conversions proceed appreciably for 3,3'-dimethoxybenzaurin at a pH of around 11. We studied the influence of nitro groups and halogens on the corresponding conversions of 3,3'-dimethoxybenzaurin.

In test tubes containing 9.5 ml of a solution of various concentrations with precisely measured pH, we introduced about 0.5 mg of an 0.0005 M alcoholic solution of the dye, after which the carefully shaken mixture was left in a dark place for 24 hours. After this interval of time, equilibrium was established between the colored anion of the dya and the colorless anion of the carbinol compound.

In control experiments, we became convinced as a result of colorimetric observations, that under the conditions of the experiment no destruction of the dye proceeded. 1 ml of the experimental solution was acidified with hydrochloric acid. Both an anion of the dye and an anion of the carbinol base thereupon were converted into the onium cation. Colorimetric determination of the latter showed that the quantity of both anions agreed in sum with the initial quantity of the dye.

TABLE 5

Dye	pH					
	10.67	10.80	10.95	11.11	11.26	11.43
3,3'-Dimethoxybenzaurin	88	68	53	40	30	23
3''-NO_2-3,3'-Dimethoxybenzaurin	20	12	5	2	0	0
4''-NO_2-3,3'-Dimethoxybenzaurin	16	8	3	1	0	0
3''-Cl-3,3'-Dimethoxybenzaurin	51.5	37	24	15	10	6
3''-Br-3,3'-Dimethoxybenzaurin	55	39	27	16	12	8
4''-Cl-3,3'-Dimethoxybenzaurin	82.5	60	43	32	24	18
4''-Br-3,3'-Dimethoxybenzaurin	85.5	62	45	34	24	18

The solutions obtained were compared according to the intensity of color with the standard solution obtained by dissolving a sample of the same weight of the dye in a borate buffer with a pH of 9.5. The results, which show the percent content of colored anion of the dye at various pH, are set forth in Table 5.

TABLE 6

Dye	pH					
	11.10	11.52	11.95	12.46	12.79	13.03
2''-Br-3,3'-dimethoxybenzaurin	100	96	81	55	33	17
2''-Cl-3,3'-dimethoxybenzaurin	100	88	67	32	16	7.5

The intensity of the color under the pH values indicated above does not change for o-halogen derivatives. The colored anions of these dyes are converted into anions of the carbinol compounds only in the presence of caustic alkalis at higher pH values, as is shown in Table 6.

TABLE 7

Substituent	H	o-Cl	o-Br	m-Cl	m-Br	p-Cl	p-Br	m-NO_2	p-NO_2
pH	10.98	12.21	12.54	10.68	10.71	10.88	10.90	~10.4	~10.3

The results obtained are portrayed graphically in Figs. 5 and 6, in which pH is plotted on the abscissa, while the percent content of the colored anion of the dye at the given pH is plotted on the ordinate.

For greater clarity, the pH values at which the content of the anion of the dye is equal to 50% are set forth in Table 7.

These data show that the content of colored anion is lowered in proportion to the increase of the concentration of hydroxyl ions, and that the given process is substantially influenced by the character and position of the substituent.

The nitro derivatives of 3,3'-dimethoxybenzaurin are distinguished by the least stability. The p-halogen derivatives are close to unsubstituted 3,3'-dimethoxybenzaurin; the m-halogen derivatives are somewhat less stable. The o-halogen derivatives, on the contrary, are distinguished by a very high stability. This, evidently, is associated with the fact that the halogen anion found in the o-position to the central carbon atom, to a certain extent shields it and thereby hinders the addition to it of hydroxyl ions and the conversion of the dye anions into the anion of the carbinol compound. To overcome this hindrance, a

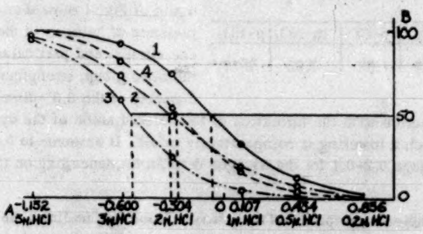


Fig. 3. A) pH (normality of HCl); B) percent content of the onium cation in the equilibrium mixture. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

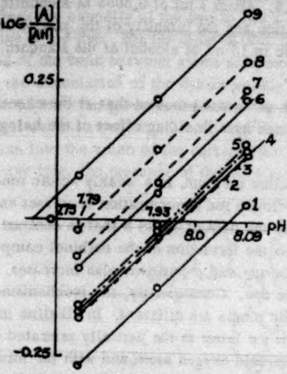


Fig. 4. Dependence of the ionization of the pigments on the pH of the medium. 1) 3,3'-Dimethoxybenzaurin; 2) m-Cl; 3) p-Cl; 4) p-Br; 5) m-Br; 6) o-Cl; 7) o-Br; 8) m-NO$_2$; 9) p-NO$_2$.

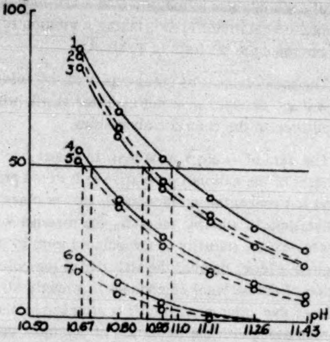


Fig. 5. Dependence of the content of colored anion of the dye on the pH. 1) 3,3'-Dimethoxybenzaurin; 2) p-Br; 3) p-Cl; 4) o-Br; 5) m-Cl; 6) m-NO$_2$; 7) p-NO$_2$.

higher hydroxyl ion concentration is necessary, and the shielding effect of bromine, with a larger atomic radius, exceeds the shielding effect of chlorine.

It turns out that the hydroxyfuchsone dyes are capable of being converted into the corresponding carbinol compounds not only in alkaline medium, but also in weakly acidic medium. The shielding action of halogens in the o-position to the central carbon atom also takes place under these conditions.

This previously unnoted property of hydroxyfuchsone dyes was detected by us for the first time during the dilution of hydrochloric acid solutions of 3,3'-dimethoxybenzaurin and its derivatives, and also during the addition of an alcoholic solution of the dye to dilute acids. We established that under these conditions, all the dyes studied by us, with the exception of the o-halogen derivatives, form, depending on the pH, almost colorless or weakly colored solutions. The o-halogen derivatives during analogous treatment yield bright yellow solutions. In all cases, however, during the addition of strong hydrochloric acid, the violet color which is characteristic of the onium cation is still produced. The measurement of the intensity of this coloration showed that the dye is not destroyed during such conversions, and that it forms an equilibrium mixture of various forms, the total of which is equal to the quantity of the initial dye.

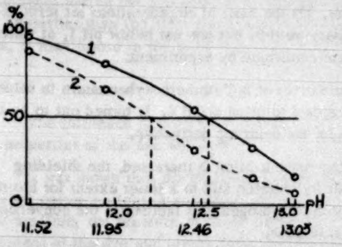


Fig. 6. Dependence of the content of colored anion on the pH. 1) o-Br; 2) o-Cl.

We assumed on this basis that during the dilution of hydrochloric acid solutions of the hydroxyfuchsone dyes there proceeds not only dissociation of the onium cation with cleavage of a proton, but also formation of the colorless carbinol compound (III), and that the relative rate of these processes depends on the structure of the dye. Preliminary experiments showed that for all the dyes, except the o-halogen dyes, a pale yellow color appeared at pH values in the range 5.5-6.5. On lowering the pH to 1, the solution again became colorless. Upon increase of the pH above 7, acid

TABLE 8

Dye		pH			
		5.89	6.11	6.34	6.50
3,3'-Dimethoxybenzaurin		2	4	6	8
m-Br-	3,3'-Dimethoxybenzaurin	4	7	11.5	19.5
m-Cl-		4.5	7.5	11.5	20
p-Br-		3.5	6	9	14.5
p-Cl-		3.5	6	9.5	15
m-NO$_2$-		6	11.5	17	22
m-NO$_2$-		13.5	23.5	31.5	37.5

dissociation began with the formation of the colored anion.

Therefore, we studied this process in the pH zone between 5.8 and 6.5. About 1 ml of 0.0005 M alcoholic solution of each dye was introduced into a test tube with 9 ml of buffer solution, and the intensity of the yellow color was measured colorimetrically, taking a solution of the same weight of dye in 10 ml of alcohol as the standard. The results obtained are set forth in Table 8.

The measurement of the intensity of the coloration of the o-halogen derivatives showed that at the experimental pH values, the dyes were not hydrated at all, which can only be explained by a shielding effect of the halogens in the o-position to the central carbon atom.

The data of Table 8 show that, in contrast to the conversions in alkaline medium, in a weakly acidic medium the content of the carbinol derivative is lowered proportionately as the hydrogen ion concentration decreases and the hydroxyl ion concentration increases. On the other hand, it is evident from the data of Table 8 that, in contrast with the conversions in alkaline medium, the presence of the nitro group hinders the formation of the carbinol compound, and increases the stability of the quinoid form of the dye. Halogens in the m- and p-positions also increases, although to a lesser degree, the stability of the colored quinoid form of the dye. Consequently, the mechanisms of formation of the carbinol compounds in strongly alkaline and weakly acidic media are different. In alkaline medium, the colored dye anion of type (IV) is attacked by the hydroxyl ion and adds the latter to the partially saturated central carbon atom, with the formation of one more negative charge on the quinoid oxygen atom, and with the formation of a colorless anion of the carbinol compound type (V). This process according to the mass action law, is accelerated during increased concentration of hydroxyl ions, to which the data of Table 5 and particularly of Fig. 5, convincingly attest. At diminished hydroxyl ion concentration, particularly with heating, the colorless anion of type (V) splits off hydroxyl and is converted back into the colored anion of type (IV).

In a weakly acidic medium it is increase not of hydroxyl ions but of hydrogen ions which facilitates the formation of the carbinol compounds even in the non-ionized state. When the pH is lowered below the isoelectric point, the coloration characteristic of the hydroxyfuchsone dye gradually disappears, the solution becomes colorless and only in the presence of a considerable increase in the acidity of the medium, when the onium cation of the dye aquires stability, does the innate color of the latter arise.

The intensity of the color characteristic of the hydroxyfuchsone dye fails to change in the pH range 5-6.5 only with the o-halogen derivatives under the influence of the shielding effect of the halogen atoms.

Conditions which counteract the shielding effect of halogens in the o-position to the central carbon atom are necessary to convert these dyes into the colorless carbinol compounds. On the basis of considerations set forth above, we assumed that a greater concentration of hydrogen ions was necessary for this, but one not below pH 1, at which the formation of onium cations is still possible. Our assumptions were confirmed by experiment.

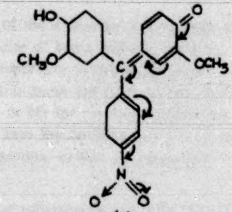
The intensity of the yellow color of solutions of o-halogen derivatives of 3,3'-dimethoxybenzaurin in solutions with a pH in the range 1-2 was compared colorimetrically with a standard solution at pH 6. It turned out to be equal on the average to 66% for the o-chloro derivative, while it was 82% for the o-bromo derivative.

It follows from these data that, actually, when the hydrogen ion concentration is increased, the shielding effect of halogens in the o-position is overcome – to a greater extent for chlorine and to a lesser extent for bromine. These data, on the other hand, confirm that an increased concentration of hydrogen ions facilitates the conversion of hydroxyfuchsone compounds into carbinol derivatives in the weakly acid zone.

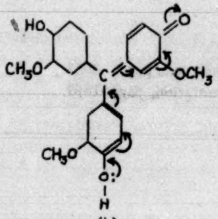
Therefore, if the formation of the carbinol compound in alkaline medium depends on the attack of hydroxyl ions, then the formation of carbinol compounds in a weakly acidic medium reduces to the hydration of molecules of the hydroxyfuchsone dye at the quinoid grouping, and the hydrogen ion concentration plays a decisive role therein.

The investigation carried out by us showed that the introduction into the benzene nucleus of 3,3'-dimethoxybenzaurin of a nitro group or of halogens influences all the indicator conversions of the dye. Under the influence of these substituents in the weakly acidic zone, the basic properties of the dye and its capacity to form onium cations are weakened and the stability of these cations is lowered. The capacity of the dye to dissociate with formation of colored anions, with corresponding lowering of the pK of dissociation is strengthened in the weakly alkaline zone under the influence of halogens and of the nitro group. In addition, these substituents influence the conversion of the dye into the corresponding carbinol compounds. In an alkaline medium, the presence of halogens and of the nitro group facilitates the formation of carbinol compounds at lower pH values. In a weakly acidic medium, these substituents, on the contrary, strengthen the stability of the dye and hinder their hydration.

Of the group of typical electron-acceptor substituents, the nitro group exerts the maximum influence, particularly when it is present in the p-position of the benzene nucleus. In drawing off electrons (scheme a), this group weakens the capacity of the dye to add a proton with the formation of an onium cation, i.e., weakens the basic properties of the dye. For the same reason, the nitro group causes the displacement of the density of the electron cloud of the bond between atoms of hydrogen and oxygen in the hydroxyl group toward the oxygen, thereby facilitating the dissociation of the dye in weakly alkaline medium with formation of the colored anion of the dye. The presence of the nitro group in the latter, by drawing off electrons, causes intensification of the positive charge on the central carbon atom, which facilitates the addition to it of a hydroxyl group at increased pH of the medium, with conversion into the anion of the carbinol derivative. During hydration in acid medium, when the hydrogen ions play a decisive role, the presence of the nitro group weakens the basicity of the dye and hampers its hydration.



(a)



(b)

In the light of these considerations, the difference between the aurin dye group from the benzaurin dye, which was noted previously [2], is understandable. In dyes of the aurin group, for example in rubrocol (b), the presence of an electron donor group in the p-position exerts an influence opposed to the influence of the electron acceptor nitro group. Rubrocol, therefore, possesses more highly basic properties, and forms onium cations which are stable at higher pH values. The rubrocol anions formed in alkaline medium also possess a greater stability and are converted into anions of the carbinol compounds only in the presence of concentrated alkali.

In the halogen derivatives of 3,3'-dimethoxybenzaurin which were studied by us, if one excludes the steric hindrances during the hydration of o-halogen derivatives, the influence of halogens, which have lesser electron acceptor properties than the nitro group, and are arranged at a distance from the hydroxy and oxo- groups in the benzene nucleus, is manifested in the same direction as that of the nitro group, but to a lesser extent.

SUMMARY

The influence of nitro groups and halogens in the benzene nucleus of 3,3'-dimethoxybenzaurin on the indicator properties of the dye was studied.

It was shown that the presence of these substituents weakens the basic properties of the dye, its capacity to form onium cations in a strongly acidic medium, and lowers the stability of the onium cations. In a weakly alkaline medium, the presence of these substituents strengthens the capacity of the dye to dissociate with the formation of anions of the dye and lowers their pK of dissociation. At increased pK values of the medium, these substituents facilitate the conversion of colored anions of the dye into the colorless anions of the carbinol compounds. Only in the o-halogen derivatives does the presence of halogens in the o-position to the central carbon atom, which shields the latter from the attack of hydroxyl groups, hamper the formation of anions of the carbinol derivatives. It was established that derivatives of 3,3'-dimethoxybenzaurin are also converted into the carbinol compounds in a weakly acidic medium; this process, in contradistinction to the formation of carbinol compounds in alkaline medium, is promoted by increased concentration not of hydroxyl ions, but of hydrogen ions. Therefore, in the presence of dilute solutions of the onium salts of the dye not only cleavage of a proton with formation of the hydroxyfuchsone dye occurs, but also hydration of the latter with decolorization of the solution. Only in the pH range between 5.5 and 6.5 in an equilibrium mixture is there an insignificant quantity of the non-hydrated dye present. The presence of halogens in the o-position to the central carbon atom, which shields the latter, also gives rise to steric hindrance during this hydration of the dye.

Of all the substituents considered above, the electron-acceptor nitro group exerts a maximum influence in all the conversions at the above indicated concentrations. Electron donor groups exert influence in the opposite direction.

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* See Consultants Bureau Translation, page 2051.

** See Consultants Bureau Translation, page 1597.

INVESTIGATION IN THE FIELD OF HYDROXYFUCHSONE DYES

XX. INFLUENCE OF THE NITRO GROUP AND HALOGENS ON THE COLOR OF DERIVATIVES OF 3,3'-DIMETHOXYBENZAURIN

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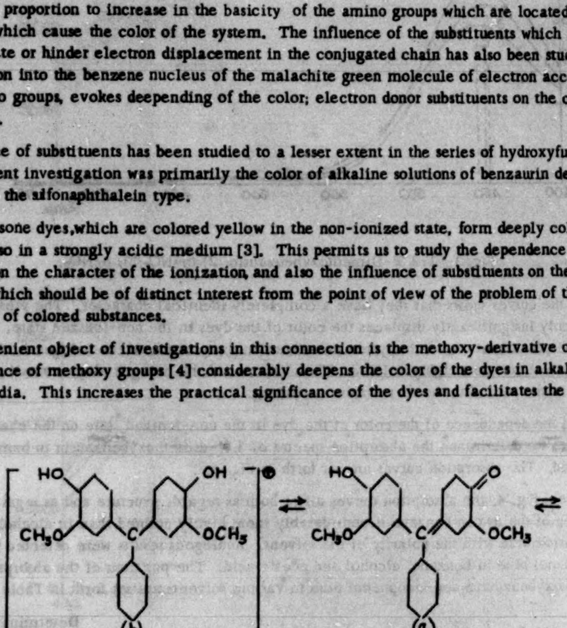
The influence of the character and position of the substituents on the color of the dye has been studied in very great detail in the series of basic triphenylmethane dyes. It has been established that a considerable deepening of the color occurs in proportion to increase in the basicity of the amino groups which are located at the ends of the conjugated bonds which cause the color of the system. The influence of the substituents which are found within this system and facilitate or hinder electron displacement in the conjugated chain has also been studied. Thus, for example, the introduction into the benzene nucleus of the malachite green molecule of electron acceptor substituents [2], particularly of nitro groups, evokes deepending of the color; electron donor substituents on the contrary, evoke diminution of the color.

The influence of substituents has been studied to a lesser extent in the series of hydroxyfuchsone dyes. The subject of the present investigation was primarily the color of alkaline solutions of benzaurin derivatives, in particular of indicators of the sifonaphthalein type.

Hydroxyfuchsone dyes, which are colored yellow in the non-ionized state, form deeply colored ions not only in an alkaline, but also in a strongly acidic medium [3]. This permits us to study the dependence of the color of the hydroxyfuchsones on the character of the ionization, and also the influence of substituents on the change of the color in various media. which should be of distinct interest from the point of view of the problem of the association between structure and color of colored substances.

A very convenient object of investigations in this connection is the methoxy-derivative of the hydroxyfuchsones, in which the presence of methoxy groups [4] considerably deepens the color of the dyes in alkaline and particularly in strongly acidic media. This increases the practical significance of the dyes and facilitates the study of their color in various media.



After having prepared the hitherto unknown nitro and halogeno derivatives of 3,3'-dimethoxybenzaurin [5, 6], we were able to study the influence of nitro groups introduced into the benzene nucleus on the color in neutral solvents, in strongly acid and in alkaline medium. The color carriers under the conditions were: the dye in the non-ionized state (a), the onium cation of the dye (b), and the anion of the dye (c).* This investigation was preceded by the study of the influence of the nitro group and halogens on the indicator properties of the dyes, described in another communication [1].

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* All the formulas given are for unsubstituted 3,3'-dimethoxybenzaurin.

The determination of the color was carried out on an automatic State Optics Institute spectrophotometer, which consisted of a double monochromator in conjunction with a photometric layout that ensured a very accurate automatic recording of the transmission curve. We carried out the photomeasurements in the visible portion of the spectrum in the 400-700mμ range at an aperture width of 4 mμ.

The determination of the color of the dyes in the non-ionized state was carried out in a 0.0001 N solution of the dye in twice redistilled ethyl alcohol. The absorption curves are depicted in Figs. 1, 2, and 3.

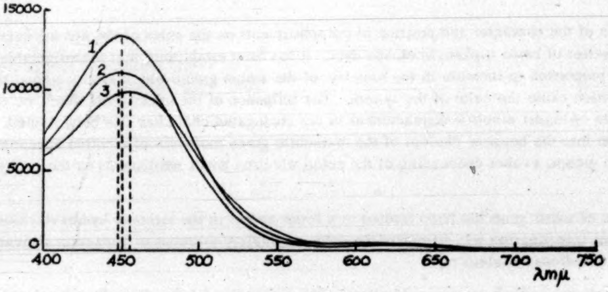

Fig. 1. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO_2; 3) p-NO_2.

Comparison of the curves shows that they have a completely identical character. The presence of nitro groups and halogens only insignificantly displaces the color of the dyes in the non-ionized state. The dependence of the degree of the displacement of the absorption maximum on the position of the halogen is clearly noticeable. The o-halogen derivatives are most highly colored. The character of the halogen plays a small role. The opposed influence of halogen in the p- and in the m-positions is striking.

We also studied the dependence of the color of the dye in the non-ionized state on the character of the solvent. With this object, we determined the absorption spectra of 3,3'-dimethoxybenzaurin in benzene, ethyl alcohol and glacial acetic acid. The absorption curves are set forth in Fig. 4.

As is evident from Fig. 4, the absorption curves differ both as regards structure and as regards position of the maximum. The solution of the dye in benzene is considerably more highly colored than in alcohol and in acetic acid, which, evidently, is associated with the polarity of the solvent. Analogous results were detected [7] during the study of the color of indophenol blue in benzene, alcohol and acetic acid. The positions of the absorption maxima of solutions of 3,3'-dimethoxybenzaurin and indophenol blue in various solvents are set forth in Table 1 for comparison.

TABLE 1

Solvent	3,3'-Dimethoxybenzaurin		Indophenol blue	
	position of the maximum (mμ)	displacement (mμ)	position of the maximum (mμ)	displacement (mμ)
Benzene	416		577	
Alcohol	451	+35	606	+29
Glacial acetic acid	455	+39	610	+33

Determination of the color of the cations (type b) was carried out in 0.00005 N solution of the dye in 15% hydrochloric acid. The absorption curves are given in Figs. 5, 6, and 7. It is evident from the figures that all the curves are similar in form, and in addition to the principal maximum, have an additional maximum in a region close to the ultraviolet portion of the spectrum, while for some dyes it passes over into this portion of the spectrum.

The presence of the nitro group, particularly in the p-position, causes the greatest bathochromic effect. With the halogen derivatives, the color is deepened in proceeding from the p-substituted to the m-substituted and particularly, to the o-substituted derivative. In all cases, the bromine derivatives were colored somewhat more deeply than the corresponding chloro derivatives.

We simultaneously studied the dependence of the color of onium cations on the character of the anion of the acid. Previously [4], in comparing the absorption spectra of solutions of 3,3'-dimethoxybenzaurin in hydrochloric and sulfuric acid with a Kōning-Martens spectrophotometer we did not find any difference between them. With the use of the more completely automatic GOI spectrophotometer, it was established that the character of the acid has some influence on the absorption spectrum of the cation formed. The absorption curves of a solution of 3,3'-dimethoxybenzaurin in 15% hydrochloric acid, in 33% sulfuric acid, in 10 and 72% perchloric acid and in 45% trichloroacetic acid are given in Fig. 8.

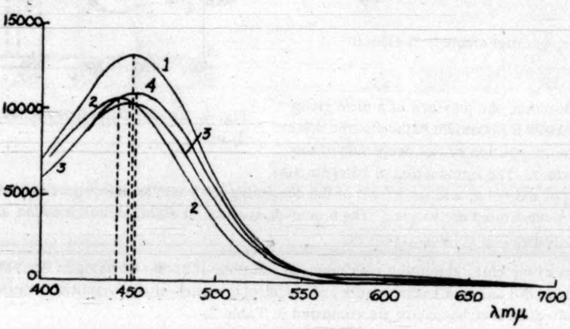

Fig. 2. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

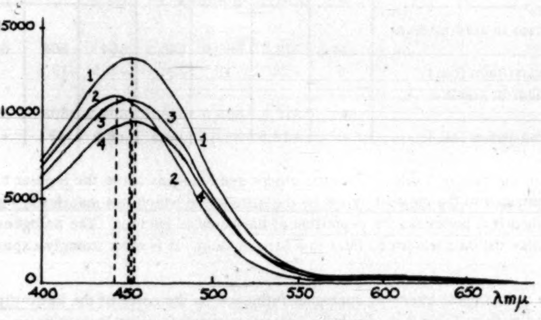

Fig. 3. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

Fig. 8 shows that in all cases, with the exception of the solution in trichloroacetic acid, the absorption spectra are identical in form and differ in the position of the absorption maxima. The solutions in sulfuric acid and in perchloric acid are somewhat more highly colored than that in hydrochloric acid. The displacement of the maximum for the solution in sulfuric acid reaches 2 mμ, while for 10% perchloric acid, it reaches 12 mμ. Trichloroacetic acid causes a deepening of the color with change in the character of the absorption curve.

The determination of the color of dye anions of type (c) was carried out in a borate buffer with a pH of 9.5. The absorption curves are set forth in Figs. 9, 10, and 11.

All these curves are identical in form, having one principal maximum in the visible portion of the spectrum and a marked supplementary maximum in the ultraviolet. Only with the o-halogen derivatives did the supplementary maximum appear in the region adjoining the ultraviolet portion of the spectrum.

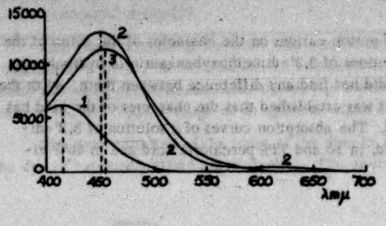

Fig. 4. 1) Benzene; 2) ethyl alcohol; 3) glacial acetic acid.

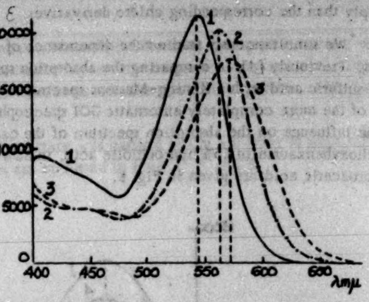

Fig. 5. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO_2; 3) p-NO_2.

In alkaline solution, the presence of a nitro group in the p-position causes a maximum bathochromic effect A nitro group in the m-position causes deepening of the color to a lesser extent. The introduction of halogens also leads to deepening of the color, and the extent of the deepening increases as one proceeds from p-substituted to m-substituted and to o-substituted derivatives. The bromo-derivatives in alkaline solutions are also colored more deeply than the corresponding chloroderivatives.

The positions of the chief absorption maximums of solutions of nitro and halogen derivatives of 3,3'-dimethoxybenzaurin in strongly acid and in alkaline media and the displacements of the maxima in comparison with solutions of unsubstituted 3,3'-dimethoxybenzaurin are compared in Table 2.

TABLE 2

Substituent	H	p-NO_2	m-NO_2	p-Cl	m-Cl	o-Cl	p-Br	m-Br	o-Br
Position of the maximum in acid medium (mμ)	544.5	572.5	563.5	548.5	554	564	549	554.5	564.5
Displacement of the maximum (mμ)	0	+28	+19	+4	+9.5	+19.5	+4.5	+10	+20
Position of the maximum in alkaline medium (mμ)	594	612.5	605.5	598.5	600.2	603	599.5	601	604
Displacement of the maximum (mμ)	0	+18.5	+11.5	+4.5	+6.2	+9	+5.5	+7	+10

It is evident from the data of Table 2 that nitro groups and halogens cause the regular bathochromic effect in all cases. It is manifested to the greatest extent by the nitro group which has manifestly electron acceptor properties, particularly when it is present in the p-position of the benzene nucleus. The halogens, which have a dual electron influence, evoke the bathochromic effect to a lesser extent. It is most strongly expressed in the o-halogen derivatives.

The nitro group and halogens exert an analogous influence on the color of the basic triphenylmethane dyes. This is visible at a glance from Table 3, in which the absorption maxima of malachite green and certain of its derivatives which contain the nitro group and halogens in the benzene nucleus are indicated [8].

TABLE 3

Substituent	H	p-NO_2	m-NO_2	o-NO_2	o-Cl
Position of the maximum (mμ)	616	637.0	635.7	633.1	630.1
Displacement of the maximum (mμ)	0	+21	+19.7	+17.1	+14.1

Similar results were obtained during the study of the influence of substituents introduced into the benzene nucleus, on the color of dyes in alkaline solutions. Sulfophthalein, which contains the sulfo group in the o-position of the benzene necleus, is more deeply colored than benzaurin, and the maximum is displaced by +6 mμ; for m- and o-bromobenzaurins the absorption maximum is also displaced by +12 and +15 mμ [9].

It is evident from what has been set forth above that in all cases involving the introduction into an unsubstituted benzene nucleus of dyes of the malachite green and benzaurin group of electron acceptor substituents, their influence leads to deepening of the color; our new experiments indicate that for hydroxyfuchsone dyes of the benzaurin

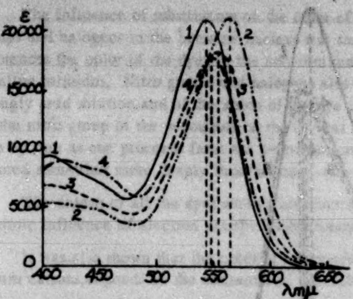

Fig. 6. 1) 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

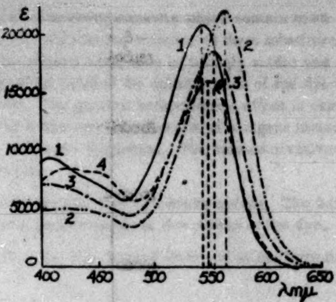

Fig. 7. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

group such an influence is manifested both in strongly acid and in alkaline medium, to a greater extent for onium cations and to a lesser extent for anions of the dyes.

It is also evident from Table 2 that both for unsubstituted 3,3'-dimethoxybenzaurin and for its nitro and halogen derivatives, the color of the anions of the dye is considerably deeper than the color of the onium cations. To explain this, Ioffe [10] put forward the hypothesis that in the anion of the dye, the color is due to oscillations of the electric charge between the terminal oxygen atoms along all the conjugated chain found between them. In the cation of the dye the migration of a positive charge is possible along the lesser conjugated chain, since in its center is located the triphenylmethane carbon atom with higher cationotropic properties than in the case of the oxygen atom. In the light of these considerations, one can understand in principle the fact that the presence in the benzene nucleus of electron acceptor groups which strengthen the cationotropic character of the central carbon atom, exerts a greater bathochromic effect on the color of the said cations of the dyes, and to a lesser extent on the color of their anions.

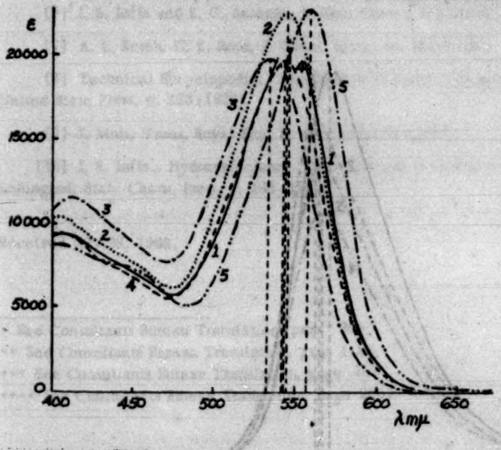

Fig. 8. 1) 15% hydrochloric acid; 2) 33% sulfuric acid; 3) 10% perchloric acid; 4) 72% perchloric acid; 5) 45% trichloroacetic acid.

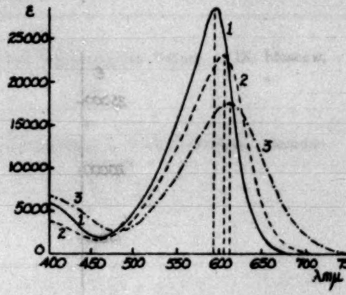

Fig. 9. 1) 3,3'-Dimethoxybenzaurin; 2) m-NO_2; 3) p-NO_2.

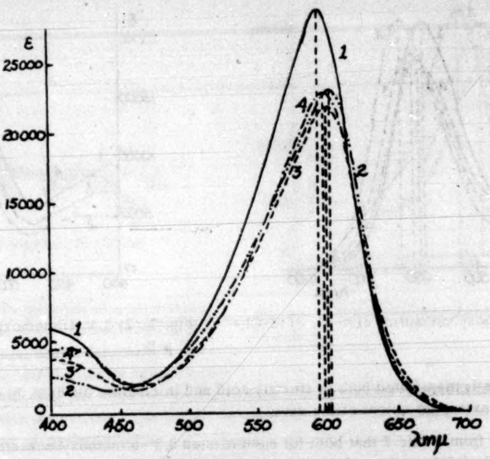

Fig. 10. 3,3'-Dimethoxybenzaurin; 2) o-Cl; 3) m-Cl; 4) p-Cl.

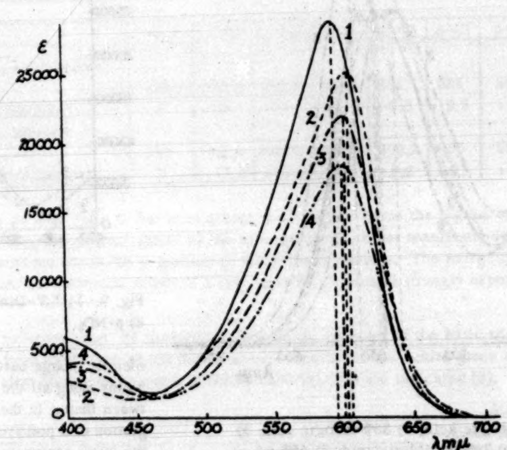

Fig. 11. 1) 3,3'-Dimethoxybenzaurin; 2) o-Br; 3) m-Br; 4) p-Br.

SUMMARY

The influence of substituents on the color of derivatives of 3,3'-dimethoxybenzaurin which contain nitro groups and halogens in the benzene nucleus was studied. It was established that the presence of these substituents influences the color of the dyes in the non-ionized state while in the ionized state, only in strongly acidic and alkaline solutions. Nitro groups and halogens also cause deepening of the color of the onium cation of the dye in strongly acid solution, and of the anion of the dye in alkaline solution. The greatest bathochromic effect is caused by the nitro group in the p-position to the central carbon atom. The bathochromic influence of halogens increases step by step as one proceeds from the p-position to the m-position and to the o-position. The bromoderivatives are colored somewhat more deeply than the corresponding chloroderivatives.

The anions of all the dyes studied are considerably more deeply colored than the onium cations. The bathochromic influence of electron acceptor substituents is manifested to a greater extent in the cations of the dye.

It was also shown that the color of hydroxyfuchsone dyes, both in the non-ionized state and in the form of onium cations, depends on the character of the solvent.

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** See Consultants Bureau Translation, page 1163.

*** See Consultants Bureau Translation, page 1597.

**** See Consultants Bureau Translation, page 2051.

CARBOXYLIC ANHYDRIDES OF AMINO ACIDS AS STRUCTURAL FRAGMENTS IN THE PROTEIN MOLECULE. II.

L. N. Akimova and N. I. Gavrilov

In the preceding communication [1] we showed not only the reality of the existence of carboxylic anhydrides of amino acids, but also a method for synthesizing them. Frānkel showed in his time [2] that amino acid anhydrides can be formed synthetically by the trypsin system, which permits us to consider their structure as presumptively "natural". Attempts to investigate the behavior of these anhydrides depending on the presence of enzymes at various concentrations of hydrogen ions were not successful. Evidently, this was a consequence of the fact that the simplest anhydrides selected by us, those of glycine and alanine, could not be compared with such anhydrides as those of tryptophane or of tyrosine. It is precisely these latter amino acids which are most labilely bound in the molecule and are of interest for the structural chemistry of protein. None-the-less, our experiments, carried out with the simplest anhydrides of glycine, shed light both on the relation of these anhydrides to the enzymes and on their stability in relation to the alkalinity of the substrates. The study of the behavior of carboxylic anhydrides in acid medium in the presence of enzymes showed a tendency toward the pepsin fermentation of these structures. The great instability of these anhydrides to high values of hydrogen ion concentration was clearly shown. This all the more underlined the necessity of studying enzymatic processes which proceed both in the direction of synthesis of the carboxylic anhydride bond and of its hydrolysis.

Attempts to prepare tyrosine or tryptophane anhydrides synthetically have not yet been successful. Nevertheless, by the study of these systems one can evidently proceed to the solution of this problem, extraordinarily important in connection with the problem of protein structure.

EXPERIMENTAL

1. Synthesis of Carbobenzoxytyrosine Anhydride

0.75 g of carbobenzoxytyrosine, prepared by Bergmann's method [3], was dissolved in 10 ml of absolute dioxane. (N-Carbobenzoxytyrosine is very excellently soluble in dioxane, alcohol and acetone). 0.4 ml of isobutyldimethylamine and 0.4 ml of chlorocarbonic ester were then added. After 10 minutes, the initially transparent solution markedly thickened (without evolution of CO_2). After having added 0.75 g more of carbobenzoxytyrosine in 10 ml of absolute dioxane, we left the reaction mixture overnight. No visible changes occurred. The precipitate was filtered off, washed repeatedly with dioxane and then with ether. The substance after having been dried in a vacuum desiccator melted at 156° and did not manifest any of the initial carbobenzoxytyrosine. The qualitative reaction with Millon's reagent was negative. It was assumed that the mixed anhydride of carbobenzoxytyrosine (at the phenolic hydroxyl group) and chlorocarbonic ester was formed. The unreacted carbobenzoxytyrosine was isolated from the dioxane filtrate.

2. Fermentation of Carbobenzoxyalanine Anhydride by Gastric Juice

a) The activity of the gastric juice was verified on a 2% aqueous gelatin solution.

b) 10 ml of 0.36% hydrochloric acid and 5 ml of gastric juice (active) were added to 0.5 ml of carbobenzoxyalanine anhydride. After having stood for 24 hours in a thermostat at a pH of 1, 0.25g of the initial anhydride was recovered and, after the filtrate had been concentrated, 0.15 g of carbobenzoxyalanine was isolated. The extent of the decomposition amounted to 30%.

c) 10 ml of 0.36% hydrochloric acid (without enzyme) was added to 0.1 g of carbobenzoxyalanine anhydride. After having stood for 24 hours in a thermostat, 0.07 g of the initial anhydride was recovered; there were traces of carbobenzoxyalanine in the filtrate. 30% hydrolyzed.

Thus, the decomposition of carbobenzoxyalanine anhydride described in experiment "b" amounts to its hydrolysis by 0.36% hydrochloric acid.

3. Fermentation of Carbobenzoxyglycine Anhydride by Gastric Juice

a) The activity of the gastric juice was verified on a 2% gelatin solution.

b) 10 ml of 0.36% hydrochloric acid and 5 ml of active gastric juice were added to 0.7 g of carbobenzoxyglycine anhydride. After standing for 6 hours in a thermostat at 37°, 0.2 g of the initial anhydride was recovered. The extent of the decomposition was equal to 71.4%.

c) 15 ml of 0.36% hydrochloric acid without enzyme was added to 0.7 g of the same anhydride. After standing for 6 hours at 37°, 0.18 g of the anhydride was recovered. 74.2% of the anhydride was hydrolyzed.

Thus, carbobenzoxyglycine anhydride is not fermented by gastric juice, but is decomposed under the influence of 0.36% hydrochloric acid for 6 hours at 37° to the extent of 72.5% (mean value of the quantities from experiments "b" and "c").

4. Fermentation of Carbobenzoxyglycine Anhydride by Trypsin

a) The activity of trypsin was verified on a 5% aqueous solution of Witte peptone.

Experiment 1. 1 ml of a 2% trypsin solution was added to 10 ml of a solution of Witte peptone. After it had stood for 6 hours in a thermostat, the solution was titrated by the Sørensen-Gavrilov method. 4.0 ml (0.15 ml in the control) of 0.2 N NaOH was consumed in the titration. 3.2 ml of 0.2 N NaOH should have been consumed theoretically. The activity of the enzyme was insignificant and was expressed in an increase in the amine groups amounting to 0.65 ml of 0.2 N NaOH.

Experiment 2. 1 ml of a 2% solution of trypsin was added to 10 ml of a solution of Witte peptone. After it had stood for 6 hours at 37° the solution was titrated by the Sørensen-Gavrilov method. 7.8 ml (0.15 ml in the control) of 0.2 N NaOH was used up in the titration. Theoretically, 3.8 ml of 0.2 N NaOH should have been consumed in the titration. The increase equal to (7.8 − 0.15 − 3.8 ml) 3.85 ml of 0.2 N NaOH showed the greater activity of this enzyme in comparison with the enzyme of Experiment 1.

b) Fermentation of carbobenzoxyglycine anhydride with trypsin in a phosphate buffer. Experiment 1 (with enzyme). 25 ml of 1/15 molar solution of buffer mixture (0.51 g of Na_2HPO_4 and 0.26 g of NaH_2PO_4) and 2 ml of a 2% trypsin solution were added to 1 g of carbobenzoxyglycine anhydride. After it had stood for 6.5 hours in a thermostat, the solution was rendered strongly acidic and 0.85 g of Na_2HPO_4 was then added. 6.5 hours after the addition of Na_2HPO_4 (in the thermostat) the precipitate was filtered off, washed on the filter with water, alcohol and ether. The precipitate obtained (0.15 g) consisted of unreacted carbobenzoxyglycine anhydride. The neutral filtrate was concentrated in a vacuum to small volume and then was acidified with hydrochloric acid to an acidic reaction. The precipitate which thereupon settled out was filtered off and washed on a filter with water. The yield of dried substance amounted to 0.55 g. According to the melting point (121°), the substance consisted of carbobenzoxyglycine [3]. Thus, 85% of the carbobenzoxyglycine anhydride decomposed.

Experiment 2 (without enzyme). 12.5 ml of 1/15 molar phosphate buffer was added to 0.5 g of carbobenzoxyglycine anhydride. After standing 6.5 hours in a thermostat at 37° a strong acidification of the medium (pH 4) was observed. 0.42 g of Na_2HPO_4 was added to the solution and left to stand in a thermostat for 6.5 hours more. The precipitate was filtered off and proved to be the initial anhydride. Its weight was equal to 0.07 g, which amounted to 14% of the carbobenzoxyglycine anhydride taken for the reaction. The neutral filtrate was concentrated in a vacuum to small volume and after acidification, the carbobenzoxyglycine was isolated.

Thus, 85% of the carbobenzoxyglycine anhydride is hydrolyzed by the action of trypsin in the course of 13 hours at 37° under the optimal conditions for its action (phosphate buffer and without it).

5. Fermentation of Carbobenzoxyglycine Anhydride by Pepsin

a) The activity of pepsin was verified on a 2% aqueous gelatin solution. Merck brand pepsin proved to be the most active of the three pepsins investigated.

b) 10 ml of 1% hydrochloric acid and 0.15 mg of active pepsin were added to 1 g of carbobenzoxyglycine anhydride. After standing for 22 hours in a thermostat, the precipitate was filtered off and repeatedly washed with water and alcohol. The weight of the substance after having been dried in a vacuum desiccator was 0.41 g, which amounted to 41% of the anhydride taken in the reaction. Thus, 59% of the carbobenzoxyglycine anhydride was decomposed. Carbobenzoxyglycine was isolated from the filtrate.

c) 10 ml of 1% hydrochloric acid (without enzyme) was added to 1 g of the carbobenzoxyglycine anhydride. After standing for 22 hours in a thermostat at 37°, 0.42 g of the initial anhydride was recovered in the manner described above. The percentage of hydrolysis of the carbobenzoxyglycine anhydride amounted to 58% in this case.

It undoubtedly follows from the data of experiment "b" that the decomposition of carbobenzoxyglycine anhydride proceeds as a result of its hydrolysis by 1% hydrochloric acid.

6. Verification of the Synthesizing Capacity of Gastric Juice (Pepsin) on Carbobenzoxyglycin Anhydride

0.1 g of glycine in 5 ml of water and in 2.75 ml of 0.2 N NaOH, and 5 ml of 2% pepsin solution (pH of the medium 4.7) were added to 0.5 g of carbobenzoxyglycine anhydride. After standing for 24 hours in a thermostat, 0.2 g of the initial anhydride was recovered from the solution while 0.2 g of carbobenzoxyglycine was isolated from the filtrate. If the synthetic reaction of the formation of carbobenzoxyglycine glycine (dipeptide) had occurred from the carbobenzoxyglycine anhydride and the glycine, then this dipeptide should have been found by its isolation in the mixture with carbobenzoxyglycine, in view of their close solubility. However, investigation of the carbobenzoxyglycine (negative biuret reaction, absence of melting point depression with synthetic carbobenzoxyglycine) showed that the formation of dipeptide does not occur in this case.

TABLE

Comparative Stability of Carbobenzoxyglycine Anhydride as a Function of the Hydrogen Ion Concentration at 37°

Enzymatic system	Duration of the action (in hrs.)	Decomposition (in %)
Gastric juice + 0.36% HCl	6	72
0.36% hydrochloric acid	6	72.5
Trypsin (phosphate buffer)	13	85
Phosphate buffer	13	85
Pepsin + 1% HCl	22	58
1% Hydrochloric acid	22	58

SUMMARY

1. In an attempt to obtain the mixed anhydride of carbobenzoxytyrosine and chlorocarbonic ester, the reaction proceeded at the phenol hydroxyl group.

2. In the trypsin and pepsin enzyme systems, enzymes which hydrolyzed the carboxyl anhydride bond were not detected (in the case of carbobenzoxyglycine anhydride).

3. The hydrolysis of glycine carboxylic anhydride proceeds most readily of all in alkaline medium and is retarded in the acid zone.

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* See Consultants Bureau Translation, page 427.

ON THE STRUCTURE OF GRAMICIDIN C

I. REDUCTION OF GRAMICIDIN C

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As yet, the structure of gramicidin C cannot be considered as established [1-7]. The hypothesis that its structure is that of a cyclopenta- or of a cyclodecapeptide is improbable since such ring compounds are evidently not encountered in nature. Attempts to synthesize similar ring compounds must be considered unsuccessful up to the present time.

The representation of gramicidin C as a common penta- or decapeptide has not proved correct, since synthetic peptides of such a structure have turned out to be slightly active antibiotically and, in contrast to gramicidin C, have an α-amino and carboxyl group.

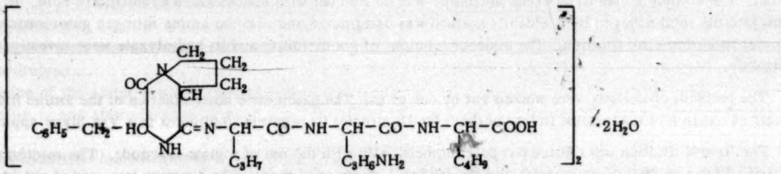
Of the numerous properties of gramicidin C it is necessary to point out the following.

1. The solubility of the antibiotic in alcohol, acetone and chloroform, which is un-characteristic of linear peptides.

2. The absence of free amine groups (except the δ-amine group of ornithine) and the practical impossibility of determining free carboxyl groups.

3. The dimer character of the gramicidin C molecule which was shown by one of us [7].

The indicated properties of gramicidin C permit one to seek its structural analogy with protein fragments. We, therefore, assume that gramicidin C has the structure of a dimer monoamidine:



Such a structure explains a number of its properties. The basic group of such amidines is not determined either by Sørensen's nor by Van Slyke's nor by Wilstätter's methods. The solubility of amidines in organic solvents is also great.

In alcoholic solution with alkali and $CuCl_2$, gramicidin C forms a violet colored biuret complex with an absorption maximum at a wave length of 570 mμ (this reaction proceeds considerably more difficultly in aqueous medium). The character of the absorption in the visible portion and the position of the maximum argue in favor of the fact that the polypeptide chain in the structure of gramicidin C is limited and contains three amino acid radicals [8]. During prolonged standing, the biuret complex of gramicidin C undergoes change — the violet color is converted into a bright raspberry color. The absorption maximum is strongly displaced toward the short wave side and is located in the 540 mμ region, which argues in favor of the appearance in the structure of a longer chain [8]. These observations on the biuret complex of gramicidin C are quite well explained by the structure assumed above.

Gramicidin C also gives an anhydride reaction with picric acid, which indicates the presence in its molecule of a piperazine ring.

The following peptides were isolated from the incomplete hydrolyzate of gramicidin C [3]: valyl-ornithine, ornithyl-leucine, leucyl-phenylalanine, phenylalanyl-proline, valyl-ornithyl-leucine, phenylalanyl-prolyl-valine, prolyl-valyl-ornithine. Thus, the following sequence of aminoacids in the gramicidin C molecule was established: phenylalanyl-propyl -valyl-ornithyl-leucyl.

Such a sequence fits into the structural formula assumed by us. Phenylalanine and proline apparently enter into the composition of the diketopiperazine type ring. The indicated amino acids are characterized by the fact that they readily form diketopiperazine rings.

The dimerization of the monoamidine can proceed according to two patterns:

1) according to Sedgewick-Syrkin-Shigorin. However, the formation during hydrolysis of the dipeptide leucyl-phenylalanine would then become incomprehensible. Further, such a dimerization should evoke the disappearance of the basic properties in the amidine group and the appearance of acidic properties in the freed carboxyl groups;

2) with the formation of an autoacylated dimer. Such an acylated amidine was studied by one of us with Akimova [9].

We shall return to the proof of the structural formula assumed by us for gramicidin C in the future. In the present work, we employed the method of electroreduction proposed by one of us with Koerina [10] to demonstrate the said structure. This method was refined by us. The gasometric determination of amine nitrogen, by Van Slyke's method, was carried out in a new apparatus proposed by one of us [12]. Potentiometric titration with a glass electrode was employed in the Sørensen micromethod. We carried out the electroreduction with a rotating mercury electrode.

EXPERIMENTAL

Gramicidin C was recrystallized from ethyl alcohol and dried in a vacuum desiccator over sulfuric acid. The substance melted at 281°.

Found %: C 55.31; H 8.04; N 13.21; Cl 4.96. $C_{30}H_{46}O_5N_6 \cdot HCl \cdot 2H_2O$. Calculated %: C 56.01; H 7.99; N 13.08; Cl 5.51.

The moisture content (determination was carried out in a drying chamber at 105°) was 2.67%.

The amine nitrogen in gramicidin C was determined gasometrically (15 minutes) and by formol potentiometric titration. The complete hydrolysis of the antibiotic was carried out with concentrated hydrochloric acid. In the hydrolyzate the total nitrogen by Kjeldahl's method was determined, and also the amine nitrogen gasometrically and by formol potentiometric titration. The aqueous solutions of gramicidin C and its hydrolyzate were investigated analogously.

The methods of analysis were worked out by one of us. The gasometric determination of the amine nitrogen was carried out in a new apparatus (micromethod) for 15 minutes (it requires 30 minutes in a Van Slyke apparatus).

The formol titration was carried out potentiometrically with the use of a glass electrode. The micromethod was verified for a number of aminoacids and for artificial mixtures of them. The titration was carried out in a pH range 7.0-9.0. However, it was later established with amino acid mixtures that it was necessary to carry out such titration in the 6.0-9.0 pH range.

The electroreduction of gramicidin C was carried out with a mercury cathode by the method which was described previously [7, 11], but with minor changes. The current density was 56 mA/cm². 50% acetic acid, to which concentrated hydrochloric acid was added for better conduction of the electrical current (40 ml HCl was added to 200 ml of 50% CH_3COOH), served as the cathode solution. The gramicidin C was dissolved in glacial acetic acid. The solution obtained, together with the wash water, was introduced into the cathode cell, after which the hydrochloric-acetic solution was added. The volume of the cathode solution was equal to 200-210 ml. The anode solution consisted of 10% hydrochloric acid. About 100 mg of the antibiotic was taken for the electroreduction. The temperature of the cathode solution was held in the 15-25° range. The duration of the electroreduction was equal on the average to 7 hours. With the object of verifying and confirming the results obtained, two parallel experiments were set up with equal samples of gramicidin C.

The course of the further treatment of the catalyzate consisted of the following. Acetic acid, water and the hydrochloric acid residue were distilled off in a water jet pump vacuum at a water bath temperature which did not exceed 30-35°.

After completion of the distilling off of the solvent, and with the object of more complete elimination of the hydrochloric acid, about 10 ml of distilled water was added three times to the dry residue and each time the distillation was renewed until complete elimination of the water added had occurred. The reduced gramicidin C was then dissolved in distilled water and the solution obtained together with wash water was transferred to a 25 ml measuring flask, after which the analysis indicated above was carried out. The solution of reduced antibiotic yielded a biuret reaction. The reaction with picric acid was negative.

In other experiments, complete hydrolysis of the reduced gramicidin C was carried out after electroreduction and distilling off the solvent. The total nitrogen was determined in the hydrolyzate by Kjeldahl's method and also the amine nitrogen gasometrically and by formol potentiometric titration. The hydrolyzate gave a negative biuret reaction and a negative reaction with picric acid.

It should be noted that the reduced gramicidin C was very excellently soluble in distilled water and concentrated hydrochloric acid, while gramicidin C is not soluble in them.

The complete hydrolysis of reduced and non-reduced antibiotic was carried out with concentrated hydrochloric acid for 39 hours in a round-bottom flask supplied with a reflux condenser. The flask was placed in a glycerine bath, the temperature of which was 115-125°.

The results of the electroreduction of gramicidin C are set forth in Table 1.

TABLE 1

Analysis of the Nitrogen Distribution of Gramicidin C Hydrochloride

Conditions of the experiment	Total nitrogen (in % of the sample)	Amine nitrogen as determined by formol titration		Amine nitrogen, determined gasometrically (15 minutes)	
		in % of the sample	in % of the total nitrogen	in % of the sample	in % of the total nitrogen
Gramicidin C prior to electroreduction and prior to hydrolysis	13.35	1.58	11.83	2.04	15.27
Gramicidin C prior to electroreduction and after hydrolysis	13.50	11.23	84.12	11.06	82.84
Gramicidin C after electroreduction and prior to hydrolysis	13.24	5.71	42.77	4.69	35.13
Gramicidin C after electroreduction and after hydrolysis	13.26	8.66	64.87	8.91	66.74
Diminution of the amine nitrogen in the hydrolyzates prior to and after electroreduction	–	2.57	19.25	2.12	16.10

Distribution chromatography on paper gave the following results:

1) Complete hydrolysis: ornithine, valine, leucine, phenylalanine (proline masked by valine);

2) after reduction, only a spot was detected which was hardly displaced;

3) complete hydrolysis after reduction (three spots): valine, leucine, ornithine (no phenylalanine; proline was absent or masked by valine).

The chromatograms confirmed our scheme for the structure of the gramicidin monomer.

In considering the formol titration data it should be noted that the figures for amine nitrogen turned out to be rather low, as a consequence of the incorrect selection of the pH range during titration (7.0-9.0). It was later established that it is necessary to carry out the titration at a pH of 6.0-9.0. It was also established that the reduction in the amine nitrogen in the hydrolyzates prior to and after the electroreduction is expressed by figures of the same order of magnitude, independently of whether hydrolyzates from pH 7.0-9.0 or pH 6.0-9.0 were being titrated.

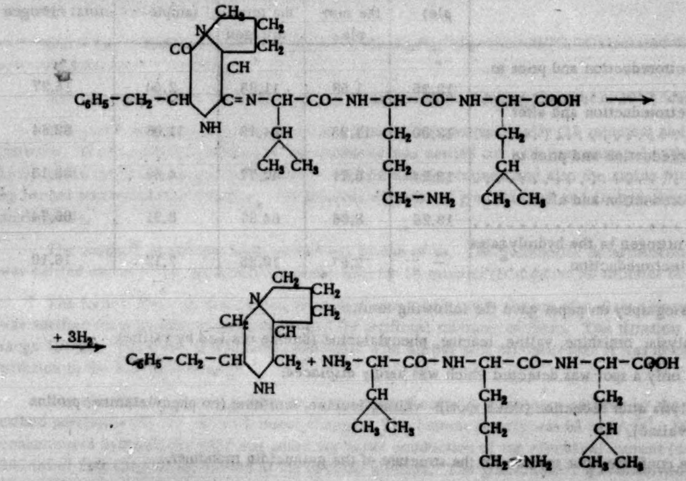
It is evident from the data of Table 1 that 2.04% of amine nitrogen or 15.27% of total nitrogen was found gasometrically in the initial gramicidin C, which is exactly equivalent to the single nitrogen atom of the δ-amino group of ornithine (theoretically, 1 nitrogen atom in gramicidin C would amount to 2.2% or 16.6% of the total nitrogen). 11.06% of amine nitrogen was found in the gramicidin C hydrolyzate. Consequently, of the 6 nitrogen atoms which enter into the gramicidin C molecule, 5 atoms have been determined. This is in complete agreement with the theoretical representations, since proline nitrogen is not determined by Van Slyke's method.

4.69% of amine nitrogen was found in the reduction of gramicidin C, which amounts to 2 nitrogen atoms. One can conclude from a comparison of the data for amine nitrogen of the reduced and non-reduced gramicidin C that after the electroreduction the amine nitrogen is doubled, i.e., after the electroreduction one more amine group can be determined. This is readily explained by the reduction reaction of gramicidin C assumed by us below, in accord with which the reduced antibiotic consists of piperazine and tripeptide fragments. There is one additional free amine group in the tripeptide besides the δ-amine group of ornithine.

8.91% of amine nitrogen, or 66.74% of total nitrogen, which is equivalent to 4 nitrogen atoms, was detected gasometrically in the hydrolyzate of reduced gramicidin C. The reduction in amine nitrogen (in comparison with the hydrolyzate of unreduced antibiotic) was equal to 2.15%, which is equivalent to 1 nitrogen atom. Actually, the hydrolysis of reduced gramicidin C leads to the cleavage of the tripeptide which forms while the acid stable piperazine is not hydrolyzed. Therefore, only 4 nitrogen atoms of the 6 nitrogen atoms in the hydrolyzate of reduced gramicidin C should be determined. This was confirmed by the experimental data. It should be noted that these considerations apply only if one assumes that proline enters into the composition of the ring, for in the opposite case, 3 nitrogen atoms should be determined in the reduced hydrolyzate of gramicidin C, i.e., the diminution of amine nitrogen should correspond to 3 nitrogen atoms, which is not actually observed.

The diminution of amine nitrogen, determinable by formol titration in the reduced hydrolyzate, is equal to 2.57% in comparison with the unreduced hydrolyzate, which also corresponds to 1 nitrogen atom. The data of the formol titration are in agreement with our assumptions concerning the structure of gramicidin C. It is only necessary to bear in mind that 50% of the piperazine is titrated by Sørensen's method [10], i.e., 1 of the 2 nitrogen atoms is determined.

Thus, the process of electroreduction of gramicidin C proceeds in the following manner:



The biuret reaction of gramicidin C was carried out under the following conditions: 0.1052 g of gramicidin C was dissolved in 14 ml of alcohol and 0.7 ml of 5 N NaOH and several drops of saturated $CuCl_2$ solution (to a volume of 15 ml) were added to the solution. After 2.5 hours, the excess $Cu(OH)_2$ was filtered off and the deep violet solution of the complex was measured spectrophotometrically with a Kolleman apparatus (Table 2). The light absorption maximum was at λ = 570 mμ. After the solution had been further kept for 35 days, a gradual change in the color was observed; it was converted into a bright raspberry color. Spectrophotometric measurement of the solution (ϵ_{II}) showed that the absorption maximum was displaced toward the short wave side.

TABLE 2

Optical Density of Copper Complexes of Gramicidin

λ	Concentration of the solution 0.56%		λ	Concentration of the solution 0.56%	
	ϵ_I	ϵ_{II}		ϵ_I	ϵ_{II}
460	0.183	0.416	580	0.698	0.560
480	0.250	0.552	600	0.640	0.415
500	0.358	0.678	620	0.568	0.310
505	–	0.710	640	0.500	0.255
510	0.422	0.740	660	0.438	0.199
540	0.610	0.790	700	0.355	0.178
550	0.665	0.745	730	0.289	0.170
560	0.699	0.689	750	0.950	0.140
570	0.708	0.690			

SUMMARY

The presence in gramicidin C of two diketopiperazine and tripeptide fragments was shown; proline was present in the first. The following peptides were in the incomplete hydrolysis products of gramicidin C: phenylalanyl-proline, phenylalanyl-prolyl-valine; consequently, phenylalanine was present in the diketopiperazine. Thus, the structural formula of the monomer of gramicidin C must be depicted as (prolyl-phenylalanyl)-2-valyl-ornythyl-leucine-amidine.

Nevertheless, for final conclusions concerning the structure of gramicidin C further investigations are necessary, in particular the isolation and identification of the hypothetical piperazine from the reaction mixture after the electroreduction is necessary. The problem of the structure of gramicidin C will be finally solved only after its synthesis.

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** See Consultants Bureau Translation, pages 341, 635, 641, 899.

*** See Consultants Bureau Translation, page 1675.

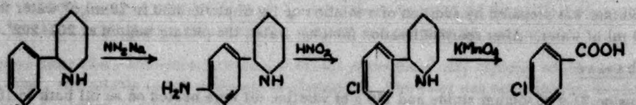
**** See Consultants Bureau Translation, page 2207, 2219.

***** See Consultants Bureau Translation, page 349.

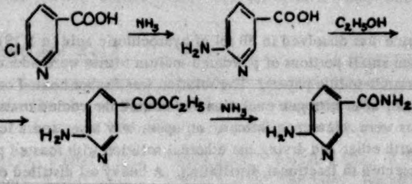
SYNTHESIS OF THE ETHYL ESTER AND AMIDE OF α_1-AMINONICOTINIC ACID

A. M. Khaletsky and L. Sh. Gurevich

Since the discovery of anabasine by Orekhov [1], many works devoted to the synthesis of derivatives of this alkaloid or products of its degradation [2] have appeared in the literature. The introduction into the pyridine nucleus of anabasine of any substituent represents a possible and rather simple method of obtaining various derivatives of α-pyridinecarboxylic acid by oxidation. Practical experience, however, showed that aminonicotinic acid derivatives were not successfully obtained in satisfactory yields by this method and, therefore, it was necessary to select other synthetic methods, in particular, the substitution of a halogen (chlorine) for the amino group with subsequent oxidation of chloroanabasine and amination of the α_1-halogen nicotinic acid



During the oxidation of α_1-chloroanabasine we isolated α_1-chloronicotinic acid, which was converted by heating with ammonia (in sealed tubes) into α_1-aminonicotinic acid. By the esterification of the latter with ethyl alcohol the ethyl ester of α_1-aminonicotinic acid was formed, which on heating with an alcoholic solution of ammonia (in sealed tubes) was converted into the amide of α_1-aminonicotinic acid according to the scheme



It was found during pharmacological investigation of the ethyl ester of α_1-aminonicotinic acid* that the latter has anesthetic activity. Since the ethyl ester of nicotinic acid does not possess anesthetic activity, the origin of its anesthetic properties must be ascribed to the introduction of the amino group in the given case.

EXPERIMENTAL

Isolation of Anabasine

a) Isolation of the alkaloids from technical anabasine sulfate by the method of Orekhov and Menshikov [3]. 2,2 kg of alkaloid mixture was obtained from 6 g of technical anabasine sulfate by extraction with ether in the presence of 3,6 kg of 30% potassium hydroxide solution.

b) Separation of anabasine from lupinine. 2.2 kg of the mixture of alkaloids was subjected to vacuum distillation: 1755 g (80% of the total mixture of alkaloids) was thereby distilled at 136-140° (12 mm). The separation of the alkaloids was carried out in three ways: 1) benzoylation of the mixture with subsequent saponification of the benzoylanabasine, 2) nitrosation of the mixture with subsequent decomposition of the nitrosoanabasine, 3) treatment of the mixture of alkaloids with hydrofluosilicic acid with subsequent decomposition of the anabasine fluosilicate. The second method turned out to be the most efficient.

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* Carried out by R. S. Konnikova.

600 g of the alkaloid mixture was dissolved in 6 liters of 10% hydrochloric acid and a 14% aqueous solution of sodium nitrite was gradually added to the solution while it was being cooled to 4°. After the addition of 2800 ml of the sodium nitrite solution, the reaction mixture was treated with a 25% potassium hydroxide solution until it had a strongly alkaline reaction; a yellow colored oily liquid thereupon separated out, which was extracted with ether. After dyring with roasted sodium sulfate and distilling off the solvent the mixture was subjected to fractional distillation. A fraction with a b.p. of 115-120° (3 mm) initially distilled over. The substance crystallized in the receiving vessel and after recrystallization from petroleum ether melted at 68-69°. A second fraction distilled over at 165-170°. 53.5 g (8.9%) of the first fraction —lupinine— was obtained and 390 g (72%) of the second —nitrosoanabasine.

225 g of the nitrosoanabasine was heated for 3 hours on a water bath with an equal volume of hydrochloric acid (sp. gr. 1.19). After cooling, the liquid was neutralized with 25% potassium hydroxide solution, and the base which was formed was extracted with ether and dried with roasted potash. After distilling off the ether and vacuum distilling at 3 mm, 175.5 g of anabasine (78% in relation to the nitrosoanabasine) was obtained.

0.2146 g sub.: 25 ml 0.0906 N HCl. 10.1 ml of 0.095 N KOH was used up in back titration. Found %: $C_{10}H_{14}N_2$ 98.44.

Anabasine picrate was prepared by addition of a solution of 1 g of picric acid in 70 ml of water to 0.25 g of anabasine in 10 ml of water. After recrystallization from hot water, the picrate melted at 201-202°.

α_1-Aminoanabasine

50 g of anabasine, 31 g of sodium amide and 150 g of vaseline oil were heated on an oil bath to 150° for 9 hours until hydrogen evolution ceased; 4.9 liters of hydrogen in all were evolved. The reaction product was treated with water, acidified with hydrochloric acid, and after separation of the aqueous layer, the filtrate was decomposed with alkali. The thick mass which formed was extracted with ether, the solution was dried with potash, the ether distilled off; the residue was vacuum distilled at 8 mm. After recrystallization from toluene, 11 g of α_1-aminoanabasine (22% in relation to the anabasine) with a m.p. of 108-109° was obtained.

0.0792 g sub.: 0.1956 g CO_2; 0.0572 g H_2O. 0.1524 g sub.: 0.3773 g CO_2; 0.1112 g H_2O. 0.0942 g sub.: 18.3 ml N_2 (10°, 766 mm). 0.0708 g sub.: 13.9 ml N_2 (12°, 766 mm). Found %: C 67.53, 67.60; H 8.10, 8.16; N 23.41, 23.48. $C_{10}H_{14}N_2$. Calculated %: C 67.79; H 8.41; N 23.72.

α_1-Chloroanabasine

18 g of α_1-aminoanabasine was dissolved in 30 ml of hydrochloric acid (d 1.19), the solution was saturated with hydrogen chloride, and then small portions of powdered sodium nitrite were added at 30-35° (the addition of the latter was regulated with starch-iodine paper). The solution was further heated on a water bath initially to 60° and then on a boiling water bath; after nitrogen evolution had ceased the cooled mass was treated with potassium hydroxide solution. Two layers were thereupon formed: an upper oily layer and a lower aqueous layer. After extracting the aqueous layer with ether and drying the ethereal solution with roasted potash, the ether was distilled off and the oily liquid was subjected to fractional distillation. A heavy oil distilled over at 134° (3 mm); it quickly crystallized and after recrystallization from gasoline 6.3 g of a substance with a m.p. of 99° (35% of the theoretical) was obtained.

0.1248 g sub.: 0.092 g AgCl. 0.1978 g sub.: 0.1411 g AgCl. 0.1130 g sub.: 13.10 ml N_2 (10°, 765 mm). 0.1410 g sub.: 16.5 ml N_2 (10°, 765 mm). Found %: Cl 18.23, 17.76; N 13.96, 14.11. $C_{10}H_{13}N_2Cl$. Calculated %: Cl 18.05; N 14.25.

α_1-Chloroanabasine consisted of colorless crystals, soluble in water (1:100), alcohol and ether.

α_1-Chloronicotinic Acid

5.5 g of α_1-chloroanabasine in 500 ml of water was oxidized with 40 g of potassium permanganate, which was added in small portions. The decolorization proceeded very quickly. The reaction mixture was filtered off from the manganese dioxide; the filtrate, after neutralization with sulfuric acid, was concentrated to small volume, and the residue acidified with 10% sulfuric acid; crystals were thereupon formed which, after having been recrystallized from hot water, melted at 199°. 3.3 g (60%) was obtained.

0.1922 g sub.: 0.1774 g AgCl. 0.2012 g sub.: 0.1812 g AgCl. 0.1828 g sub.: 13 ml N_2 (12°, 769 mm). 0.1921 g sub.: 14.4 ml N_2 (12°, 769 mm). Found %: Cl 22.21, 22.29; N 8.54, 8.99. $C_6H_4O_2NCl$. Calculated %: Cl 22.49; N 8.89.

The α_1-chloronicotinic acid consisted of colorless crystals, slightly soluble in cold water and quite soluble in alcohol and alkalis.

α_1-Aminonicotinic Acid

2 g of α_1-chloronicotinic acid was heated in a sealed tube with excess 30% ammonia solution at 170° for 8 hours; after opening the tube, the solution was concentrated until it crystallized. After filtration and washing with water and alcohol until the chlorides had been completely eliminated, the substance was recrystallized from hot water; m.p. 298-300°; the yield was 1 g, which was equivalent to 50% of the theoretical.

0.2524 g sub.: 0.4819 g CO_2; 0.0864 g H_2O. 0.3112 g sub.: 0.5924 g CO_2; 0.1201 g H_2O. Found %: C 52.09, 51.92; H 4.37, 4.31. $C_6H_6O_2N_2$. Calculated %: C 52.17; H 4.34.

Ethyl Ester of α_1-Aminonicotinic Acid

3 g of α_1-aminonicotinic acid in a mixture with 5 ml of absolute alcohol, and 3-5 ml of concentrated sulfuric acid were heated on a water bath with a reflux condenser for 9 hours. After cooling, the reaction mixture was treated with soda solution; a precipitate thereupon settled out which, after recrystallization from water, melted at 149-150°; the yield was 1.2 g (40%).

0.1032 g sub.: 0.2180 g CO_2; 0.0553 g H_2O. 0.1424 g sub.: 0.3012 g CO_2; 0.0760 g H_2O. 0.1046 g sub.: 14.3 ml N_2 (12°, 768 mm). 0.0792 g sub.: 10.8 ml N_2 (12°, 770 mm). 0.0242 g sub.: 0.5962 g camphor: Δt 12°. 0.0207 g sub.: 0.4970 g camphor: Δt 13°. Found %: C 57.62, 57.69; H 5.98, 5.97; N 16.39, 16.38. M 168.5, 159.6. $C_8H_{10}O_2N_2$. Calculated %: C 57.83; H 6.02; N 16.86. M 166.

The ethyl ester of α_1-aminonicotinic acid consisted of colorless silky crystals, which were insoluble in water, alcohol and ether, and soluble in hot water and in chloroform. The ester was saponified by heating 1 g with 5-8 ml of a 20 % aqueous solution of sodium hydroxide with a reflux condenser on a oil bath to 150° for 3 hours. A precipitate was formed during neutralization with sulfuric acid which melted at 298-300°, after recrystallization from hot water, and displayed no melting point depression in a mixed sample with α_1-aminonicotinic acid. During the addition of a solution of iodine in potassium iodide to the solution which had been rendered alkaline (after the α_1-aminonicotinic acid had been filtered off) and subsequent heating, the mixture manifested the odor of iodoform.

On saturating a 5% chloroform solution of the ethyl ester of α_1-aminonicotinic acid with hydrogen chloride, and after distilling off the solvent, a precipitate was formed which, after having been recrystallized from chloroform, melted at 191-192° and was quite soluble in water and alcohol.

0.3104 g sub.: 16 ml 0.095 N KOH. 0.2994 g sub.: 15.5 ml 0.095 N KOH. Found %: $C_8H_{10}O_2N_2 \cdot HCl$ 98.84, 99.27.

Amide of α_1-Aminonicotinic Acid

1 g of the ethyl ester of α_1-aminonicotinic acid was heated at 150-160° with a concentrated alcoholic solution of ammonia in a sealed tube for 6 hours. The reaction product was concentrated until it crystallized; after recrystallization from hot water, it melted at 312°. The yield was 0.42 g (42%).

0.2004 g sub.: 0.3840 g CO_2; 0.0897 g H_2O. 0.2212 g sub.: 0.4220 g CO_2. 0.0984 g H_2O. 0.0521 g sub.: 13.10 ml N_2 (10°, 764 mm). 0.0481 g sub.: 12.3 ml N_2 (10°, 766 mm). Found %: C 52.32, 52.04; H 5.00, 4.98; N 30.29, 30.86. $C_6H_7ON_3$. Calculated %: C 52.55; H 5.11; N 30.65.

SUMMARY

The methods of synthesizing the ethyl ester and amide of α_1-aminonicotinic acid, starting from technical anabasine sulfate, were studied. It was found that the indicated ester can be prepared by the oxidation of α_1-chloroanabasine with subsequent amination and esterification of the α_1-aminonicotinic acid which is formed. The amide of α_1-aminonicotinic acid is formed by treating the ethyl ester of α_1-aminonicotinic acid with ammonia under pressure.

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SYNTHESIS AND PROPERTIES OF AZOMETHINES FROM WEAKLY BASIC AROMATIC AMINES

B. A. Porai-Koshits and A. L. Remizov

One of the authors of the present communication and E. M. Poznanskaya [1], in the course of studying the acid hydrolysis of azomethines, concluded that this reaction proceeds via a stage of formation of an intermediate water addition product to azomethine, which consists of an amino alcohol of the structure R−CHOH−NH−R' (where R and R' are aromatic radicals).

On the other hand, Hantzsch [2] and Dimroth [3] showed in due course, that an intermediate amino alcohol of exactly the same structure is formed as a result of the addition of an amine molecule to aldehyde in the process of synthesizing azomethines. This intermediate reaction product, distinguished by a remarkable lability, depending on the conditions and the composition,is either decomposed into the initial components (i.e., amine and aldehyde), or is converted into a stable azomethine, thereby losing a molecule of water.

Since the hydrolysis of azomethines and their synthesis by the reaction of primary amines with aldehydes proceeds through a stage of formation of the same intermediate product, both these processes represent opposed directions of the same reversible reaction, which can be depicted by the scheme which follows below:

$$RNH_2 + R'CHO \rightleftharpoons R-NH-CHOH-R' \rightleftharpoons R-N=CH-R' + H_2O,$$

where R and R' are aromatic radicals.

It is ordinarily considered that all aromatic azomethines are completely stable in neutral medium and undergo hydrolytic cleavage into amine and aldehyde only in the presence of mineral acids. However, this is not actually the case. In the course of working with azomethines prepared from aromatic amines with weakly basic properties (nitroanilines, streptocidin) we were able to satisfy ourselves that such azomethines were far from inert to the action of moisture, even in the complete absence of acid.

We found, for example, that benzal-p-nitroaniline is decomposed into p-nitroaniline and benzaldehyde during any prolonged boiling of its solutions in suitable non-dehydrated polar solvents (the lower alcohols, acetone). For this very reason, its crystallization from similar solvents ultimately yields pure p-nitroaniline [1]. The sensitivity of benzal-p-nitroaniline to the action of moisture is so great that it does not resist prolonged storage in moist air. We had to observe the very same thing, although to an appreciably lesser extent in the work with benzylidine derivatives of m-nitroaniline and streptocidin (sulfanilamide). This property of azomethines prepared from weakly basic aromatic amines is direct evidence of the reversibility of the reaction resulting in their formation from the corresponding amines and aldehydes.

The position of the equilibrium of such a reaction is to the highest degree dependent, apparently, on the degree of basicity of the initial amine: the weaker its basic properties, the more strongly the equilibrium is displaced to the left,and the lower, consequently, the yield of azomethine.

As the voluminous experimental material available in the chemical literature concerning the synthesis of all kinds of azomethines shows,the reaction between primary aromatic amines and aromatic aldehydes proceeds with varying readiness, depending on the character of the aldehyde and amine components; the properties of the latter (degree of basicity) are predominate.

Aniline,and especially those of its derivatives which contain nucleophile substituents in the nucleus (OH, OAlk, Alk), react with aldehydes in the cold,and the reaction is accompanied by the evolution of heat, while amines which have a very low basicity (for example nitroanilines), react with appreciable difficulty. The directions set forth in the literature envisage in such cases the heating of the amine with a great (ordinarily two-fold) excess of the aldehyde at 150-180° until complete cessation of the evolution of water [4, 5] occurs. The azomethine thus obtained proved to be contaminated with excess aldehyde and the products of its oxidation and polymerization.

Taking into account that the reaction between primary aromatic amines and aromatic aldehydes proceeds reversibly, we accomplished the synthesis of azomethines from weakly basic amines in another manner, to wit, by eliminating the water which was formed in the reaction from its vicinity as it was formed. The need to take a considerable excess of aldehyde and to carry out the process at high temperature was thereby eliminated. The reaction was carried out in boiling toluene or xylene with simultaneous elimination of a portion of the solvent by distillation, with the vapors of which the reaction water (in the form of an azeotropic mixture) was also eliminated.

Azomethines were synthesized by this method from p- and m-nitroanilines and streptocidin (sulfanilamide) with almost quantitative yields in the presence of a minimum excess of aldehyde (5-15%). The preparations obtained were initially so pure that it was often almost unnecessary to further purify them.

EXPERIMENTAL

Benzal-p-nitroaniline. Into a reaction beaker supplied with a stirrer (with a mercury seal) and joined with the aid of a small branched fractionating column (with a thermometer) with a straight condenser, 50 ml of toluene or xylene was poured, after which 13.8 g (0.1 mole) of powdered purified p-nitroaniline was inserted while the mixture was being energetically stirred. A solution of 11.7 g (0.11 mole) of benzaldehyde in 25 ml of the given solvent (toluene or xylene) was added to the uniform suspension, which was being formed while it was being continually stirred. The beaker was then covered with a cork stopper, connected with the rest of the apparatus and, while the stirrer was operating, was heated on a glycerin bath so that boiling of the solvent, which quickly began to distill, proceeded energetically, but regularly. To facilitate the distillation, the fractionating column was initially slightly heated with a smoking gas burner flame.

The first portion of the distillate contained a large quantity of reaction water and went over at a temperature of 85-100°, the temperature then began to rise gradually. After 25 ml of moist distillate had collected in a graduated cylinder, 20 ml of fresh solvent was added to the reaction beaker (through the fractionating column) and the distillation was continued. This operation was repeated several times until 25 ml of completely transparent distillate could be collected which had distilled over at the boiling temperature of the pure solvent. After this, the addition to the reaction beaker of fresh solvent was discontinued and its contents, consisting of completely homogeneous solution, were poured out into a vessel for crystallization, where it was somewhat cooled and diluted with an equal volume of ether. The very well-formed, light yellow crystals which were evolved were separated, initially washed with benzene and then with gasoline, and dried at a temperature of 70-80°.

The yield of uncrystallized product with a m.p. of 110-115° was 20-20.5 g (88-92%).

Azomethine was obtained in a higher yield (95% and higher) in toluene than in xylene, but on the other hand, the synthesis required twice as much time (3-4 hours instead of 1.5-2 hours).

The benzal-p-nitroaniline thus obtained, recrystallized from toluene or xylene with ether, had a m.p. of 117-118° which was equivalent to the literature data [4]. It consisted of slightly yellowish, almost colorless (but not yellow as was indicated in the literature), well-formed short prisms (under the microscope), which yellowed in air as a consequence of hydrolysis, accompanied by the formation of p-nitroaniline. In alcoholic and acetone solutions it quickly decomposed and, therefore, crystallization of it from these solvents, even when rendered anhydrous in the usual way, resulted in pure p-nitroaniline.

m-Nitrobenzal-p-nitroaniline. This azomethine was prepared analogously to benzal-p-nitroaniline from p-nitroaniline and m-nitrobenzaldehyde, taken in a 5% excess in toluene with a yield of 98% of the theoretical.

After crystallization from benzene it had the m.p. of 146°, indicated for it in the literature [5].

Benzal-m-nitroaniline. The reaction between m-nitroaniline (13.8 g – 0.1 mole) and benzaldehyde (11.7 g – 0.11 mole) was carried out in boiling toluene. After completion of the elimination of the moist solvent, the hot toluene solution of the azomethine obtained was diluted with gasoline until crystallization began and cooled in ice water. The crystals which precipitated were drawn off, washed on a funnel with gasoline and dried in air.

The yield was 21 g (92-93%). M.p. 70-71°.

After crystallization from toluene with gasoline, the azomethine was obtained in the form of almost colorless needles with a m.p. of 71.5-72°, which slowly yellowed when kept in moist air. During crystallization from insufficiently well-dried non-polar solvents, it appreciably hydrolyzed. The mother liquor, after such crystallization, contained a large amount of m-nitroaniline.

Benzalstreptocidin. The preparation of benzalstreptocidin was carried out in the same apparatus and in the same manner as the above described synthesis of benzal-p-nitroaniline. However, as a consequence of the almost complete insolubility of streptocidin and its benzylidene derivative in non-polar solvents, the process of forming the azomethine was carried out in a heterogeneous medium and, therefore, required considerable time. 17.2 g of streptocidin (0.1 mole) was stirred with a solution of 12.0-12.5 g (0.113-0.118 mole) of benzaldehyde in 75 ml of xylene and the suspension which was formed was heated while being energetically stirred until the solvent boiled; this was accompanied by its slow distillation. After the reaction was completed (cessation of the distillation of moist xylene), the reaction mass was cooled, the precipitate filtered off and washed on the filter successively with benzene, ether and gasoline. The yield of crude product with a m.p. 174-177° (corrected) was around 23 g (88-89%).

Benzalstreptocidin recrystallized from dioxane or a large volume of absolute alcohol with benzene consisted of shiny snow white leaflets which slowly melted with a little decomposition at 178.0-179.2° (corrected),* were soluble in alkali with partial hydrolysis, very slightly soluble in aromatic hydrocarbons and other non-polar solvents, but considerably better soluble in pyridine, hot dioxane and benzyl alcohol. The azomethine was somewhat soluble in boiling acetone and ethanol, and underwent considerable hydrolysis in these solvents. The residue after elimination of the acetone or alcohol contained chiefly streptocidin and products of the condensation and oxidation of benzaldehyde.

SUMMARY

1. It was shown by the analysis of the condensation mechanism of primary aromatic amines with aromatic aldehydes that the process of formation of aromatic azomethines is reversible.

2. It was found that azomethines formed from aromatic amines with feebly basic properties are readily hydrolyzed under the influence of moisture even in the absence of acid, which is not characteristic of azomethines formed from comparatively highly basic aromatic amines.

3. It was concluded on the basis of the preceding that the equilibrium of the reaction involving the formation of azomethine is the more displaced toward the left (i.e., in the direction of hydrolysis) the less the basic properties of the amine which participates in it. This conclusion is confirmed also by comparison of the degree of basicity of various primary aromatic amines with data known in the literature concerning their activity in the reaction with aromatic aldehydes.

4. A method of synthesizing azomethines from weakly basic primary aromatic amines was worked out which does not require the use of a large excess of aldehyde, and which ensures a high yield and quality of the reaction product.

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* A m.p. of 174° [6] is cited in the literature for benzalstreptocidin, while according to other data it is 204° [7].

SYNTHESIS AND PHYSIOLOGICAL ACTIVITY ON PLANTS OF ISOPROPYL ESTERS OF CERTAIN ARYLCARBAMIC ACIDS

Yu. A. Baskakov and N. N. Melnikov

Together with the use of chemical agents in the fight against diseases and parasites of plants, chemical agents have obtained a rather wide use in the last few years in the struggle against weeds and as stimulators of plant growth. The scale of the use of this type of substances has continuously broadened. The most well-studied substances are used for the fight against dicotyledonous weeds as stimulators of root formation and to obtain seedless fruit [1-8]. However, great interest also attaches to another group of compounds used as herbicides in the struggle against herbaceous weeds. The simplest representative of this group of compounds is the isopropyl ester of phenylcarbamic acid, which finds use in the struggle against herbaceous weeds in the young crops of dicotyledonous plants [1, 9]. The isopropyl ester of 3-chlorophenylcarbamic acid is distinugished by an even greater activity, which several times exceeds the isopropyl ester of phenylcarbamic acid in force of action, and is more stable in the ground [10, 11].

In spite of the rather wide application of the two indicated substances in agriculture, the mechanism of the action on plants of this group of compounds has hardly been studied at all. The influence of the structure of the aromatic radical on the activity of the compound has not been studied either. It is only known that of the various esters of phenylcarbamic acid the isopropyl ester is distinguished by the strongest action on grasses [12].

A very limited number of the isopropyl esters of arylcarbamic acids containing various functional groups in the aromatic radical has been described. The most important constants have not been indicated in the literature even for the widely used 3-chlorophenylisopropylcarbamate.

In connection with what has been set forth, we undertook the present work involving the synthesis and study of the physiological activity on plants of certain isopropyl esters of arylcarbamic acids.

We accomplished the synthesis of the isopropyl esters of arylcarbamic acids by the reaction of the corresponding amines with the isopropyl ester of chlorocarbonic acid in the presence of pyridine [13].

$$ArNH_2 + ClCOOC_3H_7 + C_5H_5N \longrightarrow ArNHCOOC_3H_7 + C_5H_5NHCl.$$

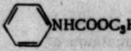
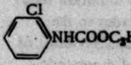
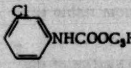
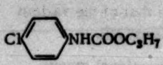
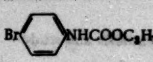
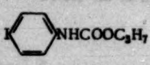
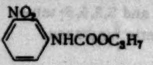
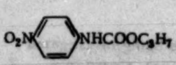
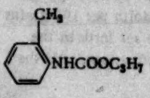
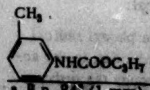
The compounds obtained by us and their properties are set forth in the table. It is of interest to note that the corresponding esters were not successfully obtained from the 2,6-dichloro-, 2,4,6-trichloro- and 2,3,5,6-tetrachloroanilines. This behavior of the enumerated amines can be explained by the presence of steric hindrance, since both positions ortho to the amino group are occupied.

The study of the physiological activity of the compounds obtained by us was carried out on wheat shoots of the Lyutescens-62 type.

100 wheat grains were treated with a determined quantity of a mixture of the substance being investigated with kaolin (carefully mixed and ground into a fine powder which passed through a No. 85 sieve), placed in a cuvette on moist filter paper and kept in a thermostat at 20-22° for 7 days. The calculation was carried out after the passage of this period. The minimum concentration of the substance which caused complete stoppage of the growth in half of the shoots was determined for all the compounds. The compounds which did not cause stoppage of the growth of the germinating grains of wheat in a concentration of 50 mg of 5% powder on kaolin per 100 grains of wheat were considered inactive. The data for the activity of the compounds studied by us are set forth in the table. The activity of the isopropyl ester of phenylcarbamic acid is set forth in the table for comparison. All the compounds synthesized by us turned out to be inactive in the tests on radish shoots.

The data obtained permit us to draw the following conclusions concerning the dependence of the physiological activity of the isopropyl esters of arylcarbamic acids on the structure of the aromatic radical.

1) Substitution for the hydrogen in the ortho- and para- positions to the amido group in the phenyl radical of the isopropyl ester of the phenylcarbamic acid by various functional groups leads to a sharp reduction in the activity of the compound. All the para- substituted phenylisopropylcarbamates were inactive; although the ortho

Structural formula	Yield (in %)	M.p. (in °)	Empirical formula	Analysis for nitrogen		Minimum concentration of the substance which caused complete inhibition of the growth in 50% of the shoots	
				found	calculated	% content in the mixture with kaolin	weight of the sample of the mixture of the substance with kaolin per 100 grains of wheat (in mg)
	–	–	–	–	–	0.025	30
	94	–*	$C_{10}H_{12}O_2NCl$	6.54; 6.32	6.54	1	30
	91	–**	$C_{10}H_{12}O_2NCl$	6.58; 6.50	6.54	0.01	30
	96	104	$C_{10}H_{12}O_2NCl$	6.43; 6.40	6.54	Inactive	–
	76	105	$C_{10}H_{12}O_2NBr$	5.49; 5.33	5.42	Inactive	–
	72	115	$C_{10}H_{12}O_2NI$	4.46; 4.43	4.60	Inactive	–
	90	91	$C_{10}H_{12}O_4N_2$	12.44; 12.20	12.50	0.5	30
	93	107	$C_{10}H_{12}O_4N_2$	12.25; 12.36	12.50	Inactive	–
	91	62	$C_{11}H_{15}O_2N$	7.32; 7.31	7.25	5	30
	82	90	$C_{11}H_{15}O_2N$	7.46; 7.21	7.25	0.025	20

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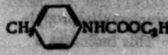
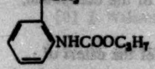
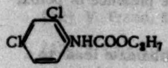
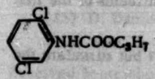
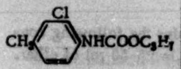
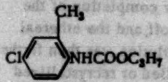
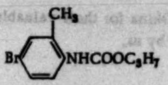
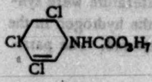
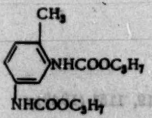
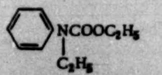
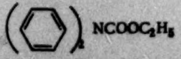
* B.p. 84° (1 mm); d_4^{20} 1.1773; n_D^{20} 1.5304.

** B.p. 112-113° (1 mm); d_4^{20} 1.1913; n_D^{20} 1.5402.

*** B.p. 127-130° (1 mm); d_4^{20} 1.1032; n_D^{20} 1.5247.

(continued)

1	2	3	4	5	6	7	8
	95	52	$C_{11}H_{15}O_2N$	7.13; 7.21	7.25	Inactive	–
	96	–***	$C_{11}H_{15}O_3N$	6.48; 6.68	6.70	5	20
	86	80	$C_{10}H_{11}O_2NCl_2$	5.82; 5.74	5.65	Inactive	–
	84	70	$C_{10}H_{11}O_2NCl_2$	5.53; 5.41	5.65	1	30
	90	40	$C_{11}H_{14}O_2NCl$	6.32; 6.17	6.15	Inactive	–
	90	113	$C_{11}H_{14}O_2NCl$	6.20; 6.31	6.15	Inactive	–
	83	27-29	$C_{11}H_{14}O_2NBr$	5.29; 5.17	5.14	Inactive	–
	88	114	$C_{10}H_{10}O_2NCl_3$	4.94; 4.92	4.96	2.5	30
	73	134	$C_{15}H_{22}O_4N_2$	9.37; 9.32	9.52	Inactive	–
	–	–	–	–	–	Stimulates growth	–
	–	–	–	–	–	Stimulates growth	–

derivatives had some physiological activity, it was, however, inferior to that of phenylisopropylcarbamate. In the series of ortho-substituted phenylisopropylcarbamates, the most active were the halogen derivatives and the least active the methyl derivatives.

It is of interest to note that parachlorophenyldimethylurea, close in structure to parachlorophenylisopropylcarbamate, has high activity and finds application as a herbicide with a selective action [14]. This indicates a different mechanism for the action on plants even of compounds which are so close in structure.

2) Substitution for the hydrogen in the meta- position to the amido group in the phenyl radical of the phenylisopropylcarbamate by substituents of the first series leads to substantial increase in the activity of the compound, while substituents of the second series lower the activity of the compound.

Such an influence of the position and character of the substituent in the aromatic radical of the esters of arylcarbamic acids on their physiological activity indicates their varying stability and behavior in plants and the different character of the reaction with enzymes. The rapid destruction of p-chloroaniline in the presence of peroxidase [15] can serve as a well-known confirmation of this.

3. The introduction of two substituents into the phenyl radical of the phenylisopropylcarbamate leads to a substantial reduction in the activity of the compound. An analogous picture is also observed in the case of the trisubstituted compounds. The reduction in the activity occurs to a lesser extent if one of the substituents of the first series is found in position 3 to the amide group.

It is of interest that diphenylethylcarbamate and ethylphenylethylcarbamate do not inhibit but stimulate the growth of wheat shoots.

EXPERIMENTAL

The preparation of the isopropyl esters of arylcarbamic acids was carried out by us under the following conditions: 0.05-0.1 mole of amine and an equimolecular quantity of pyridine were dissolved in 25-50 ml of ether and a solution of an equimolecular quantity of isopropylchlorocarbonate in 25-50 ml of ether was gradually added to the well-stirred solution obtained. The addition of isopropylchlorocarbonate was carried over the course of 10-15 minutes, after which the reaction mixture was boiled with a reflux condenser for 1 hour. After completion of the reaction, 40 ml of water was added to the reaction mixture, the aqueous layer was separated off, and the ethereal layer was washed with a 5% aqueous solution of hydrogen chloride and water. The ethereal solution was then further dried over magnesium sulfate, the ether was evaporated off and the residue was vacuum distilled or recrystallized from low boiling gasoline or petroleum ether. The compounds obtained by us and their constants are set forth in the table.

In conclusion we deem it necessary to express our gratitude to P. A. Genkel and E. Z. Okina for their valuable suggestions concerning the testing of the physiological activity of the compounds synthesized by us.

SUMMARY

A number of isopropyl esters of arylcarbamic acids which had not been described in the literature were synthesized and their activity on wheat shoots was studied. It was established that substitution for the hydrogen in the phenyl radical of the phenylisopropylcarbamate substantially influences the activity of the compound. The para- and ortho- isomers are considerably less active than the corresponding meta- isomers.

It was shown that the selective action of these compounds on monocotyledonous plants is preserved when functional groups are introduced into the phenyl radical.

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** See Consultants Bureau Translation, page 2397.

*** See Consultants Bureau Translation, page 359.

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SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS FROM HYDROCARBONS AND THEIR DERIVATIVES

III. REACTION OF ACETYLENIC HYDROCARBONS WITH PHOSPHORUS TRICHLORIDE AND OXYGEN

Yu. M. Zinovyev, L. I. Muler and L. Z. Soborovsky

It has previously been shown [1-2], that paraffinic and ethylenic hydrocarbons react with phosphorus trichloride and oxygen with the formation of the acid chlorides of alkano- and chloroalkanophosphinic acids; the reaction with chloro substituted paraffins and chloroolefins proceeds analogously.

The reaction of a number of acetylenic hydrocarbons with phosphorus trichloride and oxygen has been studied in the present work. It was preliminarily established that, similarly to the saturated hydrocarbons and olefins, neither acetylene nor other acetylenic hydrocarbons enter into reaction with phosphorus trichloride in the absence of oxygen. Equally, the reaction does not occur with phosphorus oxychloride. In the presence of oxygen, these hydrocarbons react with phosphorus trichloride with the formation of the corresponding acid chlorides of chloroalkenophosphinic acids. The reaction can be represented by the following general scheme:

$$R{-}C{\equiv}CH + 2PCl_3 + O_2 \longrightarrow RCCl{=}CHPOCl_2 + POCl_3.$$

In the reaction with acetylene along with the di-acid chloride of 2-chloroethanophosphinic acid, a crystalline substance was isolated in small quantity (m.p. 60°, b.p. 135-137° at 1 mm), the analytical data of which corresponded to those of the di-acid chloride of dichloroethanodiphosphinic acid $C_2H_2Cl_2(POCl_2)_2$. The formation of this compound, in all probability, is associated with subsequent reaction of the di-acid chloride of 2-chloroethanophosphinic acid at the multiple bond with phosphorus trichloride and oxygen

$$ClCH{=}CHPOCl_2 + 2PCl_3 + O_2 \longrightarrow C_2H_2Cl_2(POCl_2)_2 + POCl_3.$$

The reaction of phosphorus trichloride and oxygen was achieved, aside from acetylene, with hexyne-1, vinyl-and phenylacetylenes. The yield of the corresponding di-(acid chlorides), very small for acetylene, increased with increasing molecular weight of the hydrocarbon, but nevertheless remained comparatively small (for example 24% of the theoretical in the reaction with phenylacetylene).

The structure of the di-(acid chlorides) of chloroalkenophosphinic acids obtained was established (for example of the reaction products with hexyne-1 and phenylacetylene) via comparison of the properties of their derivatives with the properties of these same compounds synthesized by another method. With this object the well-known addition reaction of phosphorus pentachloride to acetylenic hydrocarbons [3] was used. The phosphorus chloroalkenotetrachlorides prepared by this method were then converted either by treatment with phosphorus pentoxide into the acid chloride of the corresponding chloroalkenophosphinic acid [4], or by hydrolysis into the free chloroalkenophosphinic acid

$$RC{\equiv}CH + PCl_5 \longrightarrow RCCl{=}CHPCl_4$$

$$3RCCl{=}CHPCl_4 + P_2O_5 \longrightarrow 3RCCl{=}CHPOCl_2 + 2POCl_3$$

$$3RCCl{=}CHPCl_4 + 3H_2O \longrightarrow RCCl{=}CHPO(OH)_2 + 4HCl.$$

The acid chlorides of chloro alkenophosphinic acids synthesized by the two methods described above were identified in the form of the aniline salts of these acids. In the determination of the melting points, a mixed sample of the aniline salts of the indicated chloroalkenophosphinic acids displayed no melting point depression.

It can, therefore, be considered as shown that the phosphorus-containing radical entering the molecule of monosubstituted acetylenic hydrocarbons adds to the carbon atom bound with the acetylenic hydrogen, i.e., forms a compound with a structure expressed by the general formula $RCCl{=}CHPOCl_2$. Thus, in the reaction under consideration, as in the reaction with ethylenic hydrocarbons, the process proceeds at the point of the multiple bond. This reaction is, apparently, a consequence of the earlier considered influence on the hydrocarbon of an intermediate addition product which arises during the oxidation of phosphorus trichloride with oxygen [2].

TABLE

Compound	Formulas of the compounds synthesized	Temperature		d_4^{20}	n_D^{20}	MR_D		Molecular weight	
		m.p. (in °)	b.p. (in °) at pressure (mm)			found	calculated	found	calculated
I	$ClCH=CHPOCl_2$	–	60-61 (1) 184-186 (750)	1.5605	1.5065	34.17	33.89	188.5	179.39
II	$ClCH=CHPO(OH)_2C_6H_5NH_2$	192-193	–	–	–	–	–	–	–
III	$C_2H_2Cl_2(POCl_2)_2$	60	135-137 (1)	–	–	–	–	–	–
IV	$C_4H_9CCl=CHPOCl_2$	–	96-97 (2.5)	1.3283	1.4981	51.97	52.36	231.6	235.49
V	$C_4H_9CCl=CHPO(OH_2)C_6H_5NH_2$	163-164	–	–	–	–	–	–	–
VI	$C_6H_5CCl=CHPOCl_2$	58-59	121-123 (2.5)	–	–	–	–	246.4	255.48
VII	$C_6H_5CCl=CHPO(OH)_2C_6H_5NH_2$	191	–	–	–	–	–	–	–
VIII	$CH_2=CHCCl=CHPOCl_2$.	–	71-73 (4)	1.4686	1.5291	43.05	42.66	209.1	205.43
IX	$CH_2=CHCCl=CHPO(OH)_2C_6H_5NH_2$. . .	186	–	–	–	–	–	–	–

In the examples described in the present work, the formation of compounds in which the $PCCl_2$ radical did not enter into the hydrocarbon at the multiple bond but as a result of the substitution of hydrogen atoms in the hydrocarbon radical was not observed. However, such processes cannot be considered excluded.

In the case of vinylacetylene containing both an ethylenic and an acetylenic bond, an organophosphorus compound is formed, the investigation ofwhich showed that it was the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid, i.e., the reaction proceeds at the point of the triple bond

$$CH_2=CH-C\equiv CH + 2PCl_3 + O_2 \longrightarrow CH_2=CHCCl=CHPOCl_2 + POCl_3.$$

This conclusion is confirmed by the data of elementary analysis, the values of the molecular weight and molecular refraction, the capacity of the substance to add four atoms of bromine and the negative reaction with Ilosvay's reagent, which indicated the absence in the molecule of a hydrogen atom at the carbon with the triple bond. In addition, the indicated structure is in accord with the well-known addition reactions to vinylacetylene [5-8]. During the hydrolysis of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid it is converted into the free acid, characterized in the form of its aniline salt. The formulas of the compounds synthesized and of the derivatives obtained from them are set forth in the table.

EXPERIMENTAL

The experiments carried out in the course of the study of the reaction of acetylenic hydrocarbons with phosphorus trichloride and oxygen were accomplished in a glass reaction vessel, supplied with a gas inlet tube with a porous plate, a socket for the thermometer and a reflux condenser. The oxygen entered into the reaction vessel from a cylinder through a rotameter. The liquid hydrocarbons were preliminarily stirred with phosphorus trichloride after which oxygen was passed through the reaction mass. A mixture of acetylene with oxygen from a gasometer was passed through phosphorus trichloride in the experiments with acetylene.

1. Reaction of Acetylene with Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chloroethanophosphinic acid (I). A mixture of acetylene with oxygen (1:1) was passed through phosphorus trichloride (435 g) at a rate of 6 liters per hour. 125 liters of the gaseous mixture was passed into the mixture. The weight of the reaction mass after the reaction was 455 g. The phosphorus oxychloride was distilled off from the reaction mixture at atmospheric pressure (temperature up to 110°). By vacuum distilling the residue, the following were isolated in insignificant quantity: a) a fraction with a b.p. of 60-61° (1 mm), d_4^{20} 1.5605, n_D^{20} 1.5065; b) a residue which congealed at room temperature.

The results of the analysis of the fraction boiling at 60-61° (1 mm):

7.71 mg sub.: 3.795 mg CO_2; 0.80 mg H_2O. 4.91 mg sub.: 2.370 mg CO_2; 0.79 mg H_2O. 0.0475 g sub.: 0.4986 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.05026 g sub.: 0.5243 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.1677 g sub.: 18.98 g benzene: Δt 0.248°. Found %: C 13.40, 13.17; H 1.4, 1.6; P 17.32, 17.21; M 182.5. $C_2H_2OCl_3P$. Calculated %: C 13.38; H 1.11; P 17.27; M 179.39.

Isolation of the acid chloride of dichloroethanodiphosphinic acid (III). The solid residue from several reactions was subjected to vacuum sublimation. The vapors from the flask for vacuum distillation were conducted through a tube heated with oil in which the temperature was maintained at 100-120°. The condensate from the tube was directed into a receiving flask. The fractional distillation was carried out at 1.5-2 mm. The 132-137° fraction was isolated and crystallized in the receiving flask. The crystals were very hygroscopic and melted around 60°.

3.34 mg sub.: 0.95 mg CO_2; 0.79 mg H_2O. 5.08 mg sub.: 1.33 mg CO_2; 1.46 mg H_2O. 0.0693 g sub.: 0.7934 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.1388 g sub.: 1.5984 g $(NH_4)_3PO_4 \cdot 12MoO_4$. Found %: C 7.61, 7.24; H 2.74, 3.12; P 18.94, 19.01. $C_2H_2O_2Cl_6P_2$. Calculated %: C 7.11; H 0.61; P 18.62.

Preparation of the aniline salt of 2-chloroethenophosphinic acid (II). 2.28 g of the acid chloride of 2-chloroethenophosphinic acid was hydrolyzed with 10 ml of water. The water and hydrogen chloride were eliminated in a vacuum.

The residue (a thick oil) was dissolved in 7 ml of ethyl alcohol, and 1.3 g of aniline in 8 ml of alcohol was added to the solution. The crystals which precipitated were separated, washed with cold alcohol and recrystallized from acetone. M.p. 192-193°.

4.70 mg sub.: 6.908 mg CO_2; 1.830 mg H_2O. 3.45 mg sub.: 5.110 mg CO_2; 1.275 mg H_2O. 0.0392 g sub.: 0.3158 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.0400 g sub.: 0.3146 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 2.895 g sub.: 0.1666 ml n_2 (24°, 744 mm). 4.823 mg sub.: 0.2744 ml N_2 (27°, 744 mm). Found %: C 40.07, 39.95; H 4.30, 4.13; P 13.32, 13.01; N 6.33, 6.42. $C_8H_{11}O_3ClNP$. Calculated %: C 40.76; H 2.97; P 13.16; N 5.94.

2. Reaction of Hexyne-1 With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid (IV). Oxygen was passed at a rate of 6 liters/hour through a mixture of 20.5 g (0.25 mole) of hexyne-1• and 151 g (1.1 mole) of phosphorus trichloride at 0-10° until evolution of heat ceased. The phosphorus oxychloride was distilled off at 40-50° (in the bath) and 40 mm. 8 g of substance which boiled at 96-97° (2.5 mm); d_4^{20} 1.3283; n_D^{20} 1.4981 was isolated from the residue after two fold redistillation.

5.13 mg sub.: 5.985 mg CO_2; 2.03 mg H_2O. 7.69 mg sub.: 8.905 mg CO_2; 2.95 mg H_2O. 0.1137 g sub.: 9.65 ml 0.1 N $AgNO_3$. 0.1144 g sub.: 9.69 ml 0.1 N $AgNO_3$. 10.22 mg sub.: 93.974 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 9.09 mg sub.: 83.842 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.2102 g sub.: 17.6 ml 0.1 N $KBrO_3$. 0.1836 g sub.: 20.16 g C_6H_6: Δt 0.2°. Found %: C 31.8, 31.6; H 4.42, 4.30; Cl•• 30.12, 29.4; P 13.36, 13.42; bromine number 66.98; M 231.6. $C_6H_{10}OCl_3P$. Calculated %: C 30.57; H 4.24; Cl•• 30.14; P 13.16; bromine number 67.9; M 235.19.

Preparation of the aniline salt of 2-chlorohexene-1-phosphinic-1 acid (V). 4 g of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid was boiled with 35 ml of water until it completely dissolved. The water was then evaporated off in a vacuum. The residue was dissolved in 5 ml of alcohol and stirred with a solution of 2.1 g of aniline in 7 ml of alcohol. The crystals which precipitated from the solution were separated, washed initially with cold alcohol, then with ether and recrystallized from acetone. M.p. 163-164°.

13.640 mg sub.: 0.883 ml 0.05 N $AgNO_3$. 11.940 mg sub.: 0.783 ml 0.05 N $AgNO_3$. 3.498 mg sub.: 0.1660 ml N_2 (24°, 746 mm) 3.500 mg sub.: 0.1617 ml N_2 (24°, 746 mm). Found %: Cl 11.50, 11.64; N 5.37, 5.21. $C_{12}H_{19}O_3NClP$. Calculated %: Cl 12.1, N 4.80.

Preparation of the acid chloride of 2-chlorohexene-1-phosphinic-1 acid from phosphorus pentachloride and hexyne-1. 16.4 g (0.2 mole) of hexyne-1 was added to a suspension of 83.4 g (0.4 mole) of phosphorus pentachloride in 150 ml of benzene which was being intensively stirred. The reaction mass was stirred for 10 hours at 30-35° and left for 30 hours at room temperature. 18.5 g of phosphorus pentoxide was then added to the reaction mixture after which the stirring was continued for 5 hours at 50°. After distilling off the benzene and the phosphorus oxychloride, the residue was fractionally distilled in a vacuum. The bulk went over at 80-100° (3 mm). During a second fractional distillation, the substance boiled at 93-95° (2 mm); d_4^{20} 1.3636; n_D^{20} 1.5059.•••

3.767 mg sub.: 4.220 mg CO_2; 1.506 mg H_2O. 4.827 mg sub.: 5.420 mg CO_2; 2.053 mg H_2O. 0.0576 g sub.: 4.94 ml 0.1 N $AgNO_3$. 12.08 mg sub.: 11.72 ml 0.1 N KOH. 17.24 mg sub.: 16.09 ml 0.1 N KOH. 0.1814 mg

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• The hexyne-1 was prepared by the method of Henne and Greenlee [9]. The substance boiled at 70-72° (literature data 71.4°).

•• Hydrolyzable chlorine (acid chloride chlorine).

••• In view of a certain discrepancy in the values for the specific gravities and indices of refraction of the samples of the acid chlorides of the chlorohexenophosphinic acids prepared, their identification was accomplished via conversion into the aniline salt. Apparently the preparation prepared according to method [3] contained a difficultly separable admixture consisting of chlorination products of hexyne-1 with phosphorus pentachloride.

sub.: 14.4 ml 0.1 N $KBrO_3$. Found %: C 30.61, 30.64; H 4.48, 4.76; Cl* 30.49; P 13.08, 12.58. Bromine number 63.5. $C_6H_{10}OCl_3P$. Calculated %: C 30.57; H 4.24; Cl* 30.14; P 13.16; bromine number 67.9.

Aniline salt of 2-chlorohexene-1-phosphinic-1 acid. The aniline salt was obtained from 1.4 g of the acid chloride prepared from phosphorus pentachloride and hexyne-1 under the conditions described above. The substance, after having been recrystallized from acetone, melted at 163°. The melting point of a mixed sample of aniline salts was 163-164°.

3. Reaction of Phenylacetylene With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chloro-2-phenylethenophosphinic acid (VI). Oxygen was passed at a rate of 8 liters per hour through a mixture of 51 g (0.5 mole) of phenylacetylene and 151 g (1.1 mole) of phosphorus trichloride at 20°. 40 liters of oxygen were passed. 417.5 g of liquid was obtained. The phosphorus oxychloride and phenylacetylene which had not reacted were distilled off at 50-60° (in a bath) and 40 mm. 22.7 g (24% of the theoretical, calculating on the basis of the phenylacetylene which had reacted) of a substance which boiled at 121-123° (2.5 mm) was isolated from the residue by fractional distillation in a vacuum. The liquid changed on standing into white crystals with a m.p. of 58-59°.

6.270 mg sub.: 8.83 mg CO_2; 1.635 mg H_2O. 3.875 mg sub.: 5.33 mg CO_2; 1.040 mg H_2O. 0.1753 g sub.: 18.9 ml 0.1 N $AgNO_3$. 11.855 mg sub.: 99.82 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 16.330 mg sub.: 138.09 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.1488 g sub.: 11.4 ml 0.1 N $KBrO_3$. 0.0707 g sub.: 15.83 g C_6H_6 Δt 0.089°. Found %: C 37.9, 38.4; H 2.92, 3.03; Cl 40.69; P 12.25, 12.29; bromine number 61.4; M 246.4. $C_8H_6OCl_3P$. Calculated %: C 37.55; H 2.34; Cl 41.68; P 12.13; bromine number 62.5; M 255.48.

Preparation of the aniline salt of 2-chloro-2-phenylethenophosphinic acid (VII). 0.9 g of the acid chloride of 2-chloro-2-phenylethenophosphinic acid was boiled with 100 ml of water for 2 hours. The water was then evaporated off in a vacuum. Crystals with a m.p. of 160° which were readily soluble in organic solvents were isolated from the concentrated solution in the course of 24 hours. The crystals were dissolved in 8 ml of alcohol and stirred with a solution of 1.3 g of aniline in 9 ml of alcohol. The aniline walt which precipitated was filtered off, washed with alcohol and ether and dried in a vacuum. White crystals were obtained which melted at 190-191°.

5.375 mg sub.: 10.505 mg CO_2; 2.345 mg H_2O. 4.390 mg sub.: 8.540 mg CO_2; 1.790 mg H_2O. 4.135 mg sub.: 0.180 ml N_2 (28°, 744 mm). 5.500 mg sub.: 0.230 ml N_2 (28°, 744 mm). Found %: C 53.08, 53.31; H 4.56, 4.88; N 4.63, 4.54. $C_8H_{15}O_3NClP$. Calculated %: C 53.93; H 4.8; N 4.40.

Preparation of 2-chloro-2-phenylethenophosphinic acid from phosphorus pentachloride and phenylacetylene (by the method of Bergman and Bondi [3]). 10.2 g (0.1 mole) of phenylacetylene was added to an intensely stirred suspension of 41.7 g (0.2 mole) of phosphorus pentachloride in 75 ml of benzene. The mixture was left for 48 hours, after which it was added to ice water in small portions. The oil which separated out was extracted with ether and after the latter had been distilled off, crystals in the form of white needles with a m.p. of 159-160° were isolated. According to Bergman and Bondi, the m.p. is 158-160°.

Preparation of the aniline salt of 2-chloro-2-phenylethenophosphinic acid. 2.1 g of 2-chloro-2-phenylethenophosphinic acid was dissolved in 5 ml of anhydrous alcohol and stirred with a solution of 1.2 g of aniline in 5 ml of alcohol. The crystals which precipitated were separated and recrystallized from alcohol; m.p. 191°.

2.955 mg sub.: 5.920 mg CO_2; 1.405 mg H_2O. 2.705 mg sub.: 5.320 mg CO_2; 1.205 mg H_2O. 5.550 mg sub.: 37.600 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 5.800 mg sub.: 37.350 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: C 53.94, 53.68; H 5.24, 4.98; P 9.85, 9.36. $C_{14}H_{15}O_3NClP$. Calculated %: C 53.93; H 4.50; P 9.95.

The melting point of a mixed sample of the aniline salts was 191°.

4. Reaction of Vinylacetylene With Phosphorus Trichloride and Oxygen

Preparation of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid (VIII). Oxygen was passed at −20 to −15° at a rate of 4 liters/hour through a mixture of 26 g (0.5 mole) of vinylacetylene and 137.5 g (1 mole) of phosphorus trichloride. 36 liters of oxygen were passed. After distilling off the phosphorus oxychloride 15.5 g (15.8%) of a substance which boiled at 70-75° (2.5 mm) was isolated from the residue. During a second fractional distillation, the substance went over at 71-73° (4 mm); d_4^{20} 1.4686; n_D^{20} 1.5291.

6.16 mg sub.: 5.265 mg CO_2; 1.325 mg H_2O. 4.56 mg sub.: 3.895 mg CO_2; 0.900 mg H_2O. 10.80 mg sub.: 4.853 ml 0.05 N $AgNO_3$. 19.92 mg sub.: 5.827 ml 0.05 N $AgNO_3$. 0.084 g sub.: 0.7000 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.0595 g sub.: 0.5122 g $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.2114 g sub.: 40.5 ml 0.1 N $KBrO_3$. 0.1621 g sub.: 18.20 g

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* Hydrolyzable chlorine (acid chloride chlorine).

C_6H_6: Δt: 0.218°. Found %: C 23.31, 23.29; H 2.4, 2.2; Cl 51.42, 51.82; P 13.78, 14.23; bromine number 153.4; M 209.1. $C_4H_4OCl_3P$. Calculated %: C 23.2; H 1.94; Cl 51.82; P 15.08; bromine number 155.6; M 205.43.

Preparation of the aniline salt of 2-chlorobutadiene-1,3-phosphinic-1 acid (IX). 1.6 g of the acid chloride of 2-chlorobutadiene-1,3-phosphinic-1 acid was heated to boiling with 25 ml of water. The water was eliminated in a vacuum. The residue was diluted with 5 ml of ethyl alcohol and stirred with a solution of 0.72 g of aniline in 5 ml of alcohol. The crystals which precipitated consisted after recrystallization from acetone of white flakes with a m.p. of 186°.

4.180 mg sub.: 6.91 mg CO_2; 2.270 mg H_2O. 2.835 mg sub.: 4.66 mg CO_2; 1.435 mg H_2O. 3.018 mg sub.: 0.1666 ml N_2 (25°, 738 mm). 4.103 mg sub.: 0.2254 ml N_2 (25°, 738 mm). Found %: C 45.08, 44.83; H 6.08, 5.66; N 6.14, 6.11. $C_{10}H_{13}O_3NClP$. Calculated %: C 45.88; H 4.97; N 5.35.

SUMMARY

The reaction involving the formation of organophosphorus compounds by the reaction of hydrocarbons or their derivatives with phosphorus trichloride and oxygen which had been previously described for paraffinic and ethylenic hydrocarbons and their chlorosubstituted derivatives, was extended to acetylenic hydrocarbons. The reaction was accomplished with acetylene, hexyne-1, phenylacetylene and vinylacetylene. The corresponding acid chlorides of chloroalkenylphosphinic acids with the general formula $R-CCl=CHPOCl_2$ were isolated and characterized.

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INVESTIGATIONS IN THE 1,2-NAPHTHO-(3',4')-FURAZAN SERIES

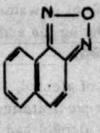
II. NITRATION AND CHLORINATION OF 1,2-NAPHTHO-(3',4')-FURAZAN

S. V. Bogdanov and S. F. Petrov

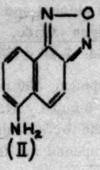
According to the data of Green and Rowe [1], the nitration of 1,2-naphtho-(3',4')-furazan (I) by cooling with a 40% excess of nitric acid yields only one mononitro compound with a m.p. of 143°. This substance is stable to alkali, but is oxidized by chromic acid to 3-nitrophthalic acid. The authors assumed that the nitration product was 5- or 8-nitronaphthofurazan. With an increased excess of nitric acid, a mixture of the dinitrocompound with a small quantity of mononitro compound with a m.p. of 147° is formed. Both the dinitrocompound and the mononitrocompound are decomposed by boiling dilute alkali. A 3- or 4-nitronaphthofurazan structure is indicated for the mononitro compound, while for the dinitrocompound a 4 (or 3), 5 (or 8)- dinitronaphthofurazan structure is indicated. Nothing has been communicated concerning attempts to determine the structure of the nitrocompounds.

We obtained the nitrocompound under the conditions recommended by Green and Rowe for the nitration of naphthofurazan to 5- or 8-nitronaphthofurazan in yields exceeding that theoretically possible. It was, evidently, a mixture of the mononitro and dinitro compounds. The nitration product, prepared with the theoretical quantity of nitric acid, did not have a sharp melting point after washing with alkali and crystallization. It proved possible to convert it into an amino compound without disturbing the furazan ring. The reaction proceeded smoothly by reducing with iron in the presence of hydrochloric acid or of stannous chloride and was somewhat complicated by side reactions when sodium sulfite was used.

The reduction product proved to be a mixture of amino compounds, from which were isolated 5-aminonaphthofurazan (II) and 7-aminonaphthofurazan (III). The quantity of pure 7-aminonaphthofurazan isolated amounted to 39.6% and of the 5-isomer 26.6% of the total amino compounds. Both amino compounds were yellow colored and their salts were colorless and readily decomposed with water.



(I)



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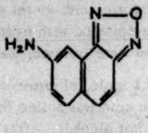

(III)

The structure of 7-aminonaphthofurazan was established by converting it (via the diazocompound) into hydroxynaphthofurazan and comparison of the latter with the 7-hydroxynaphthofurazan, obtained from 1-nitroso-2,7-dihydroxynaphthalene [2].

To demonstrate the structure of 5-aminonaphthofurazan the amino compound was converted via the diazocompound into a sulfonic acid; the latter was compared with naphthofurazan-5-sulfonic acid obtained from 2-naphthylamine-5-sulfonic acid via 2-naphthol-5-sulfonic acid and 1-nitroso-2-naphthol-5-sulfonic acid.

Consequently, the nitration of naphthofurazan during cooling, contrary to the assertion of Green and Rowe, leads to at least two compounds – 5-nitro- and 7-nitronaphthofurazan.

The 7-chloronaphthofurazan was prepared from 7-aminonaphthofurazan, while the 5-chloro- and 5-hydroxynaphthofurazans were prepared from 5-aminonaphthofurazan.

The monochloro derivative was formed by the chlorination of fused naphthofurazan in the presence of iron. This same substance was prepared by the action of potassium chlorate on a hydrochloric acid solution of naphthofurazan-3-sulfonic acid. Consequently, the direct chlorination of naphthofurazan yields 3-chloronaphthofurazan.

It can be noted that the sulfonation of naphthofurazan at 20° also led to substitution in the 3-position [3].

On treatment with potassium chlorate naphthofurazan-4-sulfonic acid in hydrochloric acid solution, similarly to 3-sulfonic acid, exchanges the sulfonic group for chlorine and is converted into 4-chloronaphthofurazan.

EXPERIMENTAL

Naphthofurazan was prepared by the action of sodium hydroxide on the bisulfite compound of 1,2-naphthoquinonedioxime [4] or by the oxidation of 1-nitroso-2-naphthylamine. The latter was prepared by treating 1-nitroso-2-naphthol with ammonia [5].

The reaction was carried out in an open flask by passing gaseous ammonia through a solution of nitrosonaphthol in aqueous ammonia which was heated to 90-94°. The yield of material, cleaned by reprecipitation from hydrochloric acid, was 75% of the theoretical. Oxidation of the nitrosonaphthylamine was carried out by pouring a 5% solution of sodium hypochlorite (20% excess) into a suspension of nitrosonaphthylamine in a 10 fold quantity of 10% sodium hydroxide solution which was cooled to 0-5°; the yield of naphthofurazan, purified by steam distillation (m.p. 79°) was 88% of the theoretical. Similar results were obtained by substituting potassium ferricyanide for the hypochlorite.

Nitration of naphthofurazan. In the Green and Rowe preparation of the mononitro compound a mixture of 3.6 ml of 95% nitric acid and 15 ml of concentrated sulfuric acid was added to a cooled solution of 10 g of naphthofurazan in 100 ml of concentrated sulfuric acid. In our experiments the nitrating mixture was introduced at −2 to 0° for 40-75 minutes, the mass was stirred at 0° for 4 hours more and diluted with ice to a sulfuric acid concentration of 30-32%. The white precipitate of the nitro compound which settled out was filtered and washed with water, dilute soda solution, and again with water.

15.7 g of the nitro compound (theoretical yield of mononitro compound 12.6 g) was obtained from 10 g of naphthofurazan. Subsequently, the theoretical quantity of a 2% excess of nitric acid was used; traces of unchanged naphthofurazan remained. The water-washed nitration product, 68 g of naphthofurazan, was stirred for 30 minutes at 90-95° with 750 ml of a 7.5% solution of sodium hydroxide, filtered and subjected to analogous treatment once more. The alkali was colored during the first treatment, a dark brown color, and during the second – a pale yellow color. The yield was 79.9-81.6 g; i.e., 93-95% of the theoretical. The substance had a light brown color, melted in the 132-155° range, was readily soluble in dichloroethane, acetic acid and benzene; crystallized from alcohol in the form of colorless needles with a m.p. of 138-144°.

Reduction of the nitronaphthofurazan. a) A mixture of 3 g of nitronaphthofurazan, 20.7 g of 76% stannous chloride, 39 ml of 31.5% hydrochloric acid, 80 ml of alcohol and 80 ml of water was boiled for 3 hours. After adding hot water, the tin was precipitated with hydrogen sulfide. During the addition of ammonia to the filtrate, yellow flakes of amino compound were isolated; yield: 2.15 g (83.2%).

b) A mixture of 21.5 g (0.1 mole) of nitrocompound, 500 ml of alcohol, 86 ml of water, 20 g of iron shavings and 1.5 ml of 32.5% hydrochloric acid was boiled for 6 hours. After precipitating the iron with soda, the sludge was filtered off and washed with hot alcohol. After the bulk of the alcohol had been distilled off from the filtrate, the filtrate was diluted with water and the amino compound was filtered off. The yield was 15.83 g (85.6%).

c) 372 ml of sodium sulfide solution containing 62.1 g of sodium sulfide was poured into a boiling suspension of 81.5 g of the nitrocompound in 1400 ml of alcohol, in one batch, and the mixture was boiled for 3.5 hours. After distilling off the alcohol the precipitate was filtered; the weight of the precipitate was 66.8 g. It contained 14% of admixture which was not soluble in hydrochloric acid, alkalis or in the usual organic solvents. This admixture dissolved in sulfuric acid with a red coloration and was re-isolated with water in the form of fine, bent yellow needles; it melted in the 190-220° range; contained nitrogen and did not contain sulfur. By increasing the duration of the reduction to 16 hours, the quantity of admixture was not changed, while by substituting sodium disulfide for the sulfide, it was somewhat diminished.

The amino compound obtained in these experiments melted at 132-160°, and did not yield a substance with a sharp melting point on recrystallization.

Separation of the amino compounds. 17.52 g of the amino compound obtained by the reduction of 21.5 g of the nitrocompound with sodium disulfide was boiled with 2100 ml of 4% hydrochloric acid, the insoluble residue was filtered and washed with hot 4% hydrochloric acid and with water. The weight of the residue was 1.55 g, i.e., 8.8% of the quantity of mixture taken. The hydrochloride of the amino compound precipitated when the filtrate was cooled to 40-45°. The amino compound which was isolated from this salt melted at 156-160°. After twofold crystallization of the hydrochloride from hydrochloric acid, 7-aminonaphthofurazan with a m.p. of 161.2-161.5° was isolated. It was readily soluble in benzene and dichloroethane, crystallized from alcohol in the form of yellowish needles with a green fluorescence. The hydrochloride consisted of colorless leaflets.

4.132 mg sub.: 0.837 ml N_2 (21°, 738 mm). Found %: N 22.84. $C_{10}H_7ON_3$. Calculated %: N 22.70.

A yellow precipitate with a m.p. of 141-178° was isolated from the filtrate from the hydrochloride by addition of ammonia. After threefold crystallization of it from alcohol, yellow needles of 5-aminonaphthofurazan with a m.p. of 208.3-208.7° were isolated, which were readily soluble in benzene and dichloroethane. The hydrochloride consisted of short colorless prisms.

3.880 mg sub.: 0.819 ml N_2 (27°, 715 mm). Found %: N 22.57. $C_{10}H_7ON_3$. Calculated %: N 22.70.

The mixture of amino compounds isolated from the alcoholic filtrate after purification of the 5-amino compound, was again separated with hydrochloric acid. A total of 6.32 g (36.1% of the initial mixture) of 7-amino compound and 4.25 g (24.3% of the initial mixture) of 5-amino compound was isolated; 1.35 g of the mixture remained unseparated.

7-Chloronaphthofurazan. A solution of 2.08 g of sodium nitrite and 25 ml of sulfuric acid was poured into a solution of 4.62 g (0.025 mole) of 7-aminonaphthofurazan in 25 ml of concentrated sulfuric acid at −1°. The solution was stirred for 3 hours and diluted with ice to a concentration of 50% sulfuric acid. After eliminating the excess nitrogen oxides with urea, the diazo compound was poured into a solution of cuprous chloride in a mixture of 120 ml of 36.3% hydrochloric acid and 40 ml of water which was heated to 70-80°. The orange precipitate which settled out was a compound of chloronaphthofurazan with copper salt, to eliminate which it was twice boiled for 1 hour with 250 ml of 10% hydrochloric acid; the yield was 4.82 g. It consisted of colorless needles (from aqueous alcohol), m.p. 132.7-133.2°. It was quite soluble in organic solvents.

3.368 mg sub.: 0.415 ml N_2 (24°, 732 mm). 26.534 mg sub.: 6.491 ml 0.02 N $AgNO_3$. Found %: N 13.62; Cl 17.35. $C_{10}H_5ON_2Cl$. Calculated %: N 13.70; Cl 17.33.

7-Hydroxynaphthofurazan. The diluted solution of the diazo compound obtained as above from 4.62 g of 7-aminonaphthofurazan, was poured into 150 ml of boiling 50% sulfuric acid. The mixture was cooled, the precipitate filtered and reprecipitated from dilute sodium hydroxide; the yield was 4.23 g. It consisted of almost colorless needles (from aqueous alcohol), m.p. 217.5-218°. It was quite soluble in alcohol and benzene; alkaline solutions of it had an orange color.

3.680 mg sub.: 0.498 ml N_2 (22°, 725 mm). Found %: N 14.94. $C_{10}H_6O_2N_2$. Calculated %: N 15.05.

Methoxy compound. It was obtained by heating an alkaline solution of the hydroxy compound with dimethyl sulfate. It consisted of colorless needles (from aqueous alcohol), m.p. 129.8-130.2°. It was quite soluble in alcohol and benzene.

Acetoxy derivative. It was obtained by heating the hydroxy compound with acetic anhydride. It consisted of colorless needles (from aqueous alcohol), m.p. 137.0-137.4°. It was quite soluble in alcohol, benzene and acetic acid.

The 7-hydroxynaphthofurazan used for comparison was obtained by the exchange method of Nietzki and Knapp [2]. 4.73 g (0.025 mole) of 1-nitroso-2,7-dihydroxynaphthalene was dissolved in 6.32 g of 95% sodium hydroxide in 50 ml of water; 3.48 g of hydroxylamine hydrochloride was added and the liquid was boiled for 1 hour. 13 ml of 38% sodium hydroxide was added to the solution and the boiling was continued for 1 hour more. The cooled solution was diluted with 30 ml of water and the hydroxy compound was precipitated with hydrochloric acid. The yield was 3.04 g . It consisted of almost colorless needles (from aqueous alcohol), m.p. 218-218.3°. The mixture of the substance with hydroxynaphthofurazan obtained from the amino compound, melted at 218-218.3°. The acetoxy derivative consisted of needles (from aqueous alcohol), m.p. 136.7-137°; a mixture of the acetoxy derivatives melted at 137-137.3°.

5-Chloronaphthofurazan. It was prepared analogously to 7-chloronaphthofurazan from 4.62 g of 5-aminonaphthofurazan. In the given case, the chloroderivative at once precipitated in the free state and did not require treatment with hydrochloric acid. The yield was 4.75 g. It consisted of colorless needles (from aqueous alcohol), m.p. 120.2-120.8°. It was quite soluble in organic solvents.

3.380 mg sub.: 0.428 ml N_2 (27°, 728 mm). 24.041 mg sub.: 5.88 ml 0.02 N $AgNO_3$. Found %: N 13.80; Cl 17.34. $C_{10}H_5ON_2Cl$. Calculated %: N 13.70; Cl 17.33.

5-Hydroxynaphthofurazan. It was prepared analogously to the 7-hydroxy compound by the decomposition of the diazo compound from 4.62 g of 5-aminonaphthofurazan; the yield was 4.07 g. It consisted of yellow needles (from aqueous alcohol), m.p. 220.6-221.1°. It was quite soluble in organic solvents; alkaline solutions of it had an orange color.

3.247 mg sub.: 0.444 ml N_2 (25°, 733 mm). Found %: N 15.11. $C_{10}H_6O_2N_2$. Calculated %: N 15.05.

Methoxy derivative. It consisted of slightly yellowish needles (from alcohol), m.p. 159.1-159.5°.

Naphthofurazan-5-sulfonic acid. A solution of 2.16 g of sodium nitrite in 25 ml of sulfuric acid was poured into a solution of 4.62 g of 5-aminonaphthofurazan in 35 ml of concentrated sulfuric acid cooled to 3-4°. After stirring for 4 hours, the mixture was diluted with 270 g of ice and the excess nitrogen oxides was eliminated with urea. The solution of diazo compound was poured at 0-3° over a period of 5 minutes into a mixture of 38 ml of concentrated sulfuric acid, 400 ml of water and 46.5 g of 80.6% freshly prepared by Gattermann's method [6], copper paste which had been saturated with sulfur dioxide. A stream of sulfur dioxide was maintained while the diazo compound was being added. After stirring for an hour, the copper precipitate and the sulfinic acid were filtered off and heated to 95° with soda solution. 7 ml of 30% hydrogen peroxide was added to the filtered solution and after stirring for 2 hours the residue of hydrogen peroxide was decomposed with manganese dioxide. The solution was concentrated and the sodium salt of the sulfonic acid which precipitated was filtered; the yield was 5.3 g. It consisted of colorless needles, quite soluble in hot and poorly soluble in cold water.

0.3371 g sub.: loss on drying (150°) 0.0472 g. 0.3156 g sub.: 0.0714 g Na_2SO_4. Found %: H_2O 14.00; Na 7.32. $C_{10}H_5O_4N_2SNa \cdot 2.5H_2O$. Calculated %: H_2O 14.19; Na 7.25.

Sulfochloride. It was obtained by heating a mixture of the sodium salt of the sulfonic acid with phosphorus pentachloride on the water bath. It was poorly soluble in benzene. It consisted of colorless needles or elongated rhombs (from dichloroethane), m.p. 116.5-117.2°.

Amide. It consisted of prisms (from alcohol), m.p. 235.8-236.2°.

3110 mg sub.: 0.469 ml N_2 (23°, 735 mm). Found %: N 16.81. $C_{10}H_7O_3N_3S$. Calculated %: N 16.86.

Synthesis of Naphthofurazan-5-sulfonic Acid From 2-Naphthol-5-sulfonic Acid

2-Naphthol-5-sulfonic acid. The pressed-out paste of the diazo compound obtained from 97.8 g (0.4 mole) of 91.3% 2-naphthylamine-5-sulfonic acid, was introduced over a period of 35 minutes into 500 ml of boiling 20% sulfuric acid. The dark red solution was neutralized with barium hydroxide and a solution of soda was poured into the solution obtained, after separating out the barium sulfate, to convert the barium salt of the sulfonic acid into the sodium salt. By partial concentration of the filtrate, 87 g 61% sodium salt of the sulfonic acid was isolated from the barium carbonate. It was quite soluble in water and crystallized in the form of long, colorless hexagonal flakes.

0.5130 g sub.: loss on drying (140°) 0.1148 g. 0.3347 g sub.: 0.0738 g Na_2SO_4. Found %: H_2O 22.38; Na 7.15. $C_{10}H_7O_4SNa \cdot 4H_2O$. Calculated %: H_2O 22.63; Na 7.23.

1-Nitroso-2-naphthol-5-sulfonic acid. It was prepared analogously to 1-nitroso-2-naphthol-7-sulfonic acid [7]. The sodium salt was quite soluble in hot water and crystallized in the form of yellow needles.

0.4960 g sub.: loss on drying (120°) 0.1034 g. 0.3061 g sub.: 0.0621 g Na_2SO_4. Found %: H_2O 20.84; Na 6.57. $C_{10}H_6O_5NSNa \cdot 4H_2O$. Calculated %: H_2O 20.73; Na 6.63.

Naphthofurazan-5-sulfonic acid. A mixture of 27 ml of 48.8% sodium hydroxide and 73 ml of water and then 14 g of hydroxylamine hydrochloride was added to a suspension of 34.7 g (0.1 mole) of the sodium salt of the nitroso compound in 100 ml of water. The solution was kept at 20° for 1 hour and boiled for 20 minutes. The sodium salt of the sulfonic acid which precipitated on cooling was filtered; yield 28.9 g. It consisted of colorless needles (from water).

0.2665 g sub.: loss on drying (150°) 0.0372 g. 0.2596 g sub.: 0.0581 g Na_2SO_4. Found %: H_2O 13.96; Na 7.25. $C_{10}H_5O_4N_2SNa \cdot 2.5H_2O$. Calculated %: H_2O 14.16; Na 7.25.

Sulfochloride. It consisted of colorless needles (from toluene), m.p. 118-118.3°. A mixture with the sulfochloride obtained via the 5-amino compound, melted at 117.2-117.8°.

Amide. It consisted of prisms (from alcohol), m.p. 236-236.3°. A mixture of the substance with the amide obtained via the 5-amino compound, melted at 236.0-236.3°.

3-Chloronaphthofurazan. a) Chlorine was passed into a mixture of 13.6 g (0.08 mole) of naphthofurazan and 0.14 g of iron powder at 78-80°. After an hour, the formation of crystals of the chloroderivative began and the mass solidified. The reaction product was introduced into a dilute soda solution, the mixture was heated to boiling, cooled, the precipitate filtered off and washed with water. The weight of the precipitate was 16.3 g, m.p. 113-131°. The precipitate was dissolved in 150 ml of hot acetic acid, 9.05 g of chloronaphthofurazan was isolated while the solution was cooled, 3.05 g more was isolated by diluting the filtrate with water; the total yield was 12.1 g, m.p. 138-142°. 1.36 g of unchanged naphthofurazan with a m.p. of 75-78.5° was isolated during further dilution of the filtrate.

It consisted of colorless needles (from alcohol or acetic acid), m.p. 144.2-144.8°. It was quite soluble in alcohol and less so in acetic acid.

44.252 mg sub.: 10.91 ml 0.2 N $AgNO_3$. Found %: Cl 17.48. $C_{10}H_5ON_2Cl$. Calculated %: Cl 17.33.

b) A solution of 1.47 g of potassium chlorate in 20 ml of water was added to a boiling solution of 2.99 g (0.01 mole) of the sodium salt of naphthofurazan-3-sulfonic acid in 160 ml of water and 5.6 ml of 35% hydrochloric acid, in the course of 3 hours. Several minutes after the beginning of the addition, white needles of chloronaphthofurazan began to precipitate. The mixture was boiled for 1 hour more, cooled, and the precipitate was filtered. The yield was 1.77 g (86.5%). M.p. 144-145.5°. It consisted of colorless needles (from alcohol), m.p. 144.8-145.5°. The melting point of the mixture of chloronaphthofurazans was 144.6-145.5°.

3.248 mg sub.: 0.399 ml N_2 (21°, 732 mm). 39.021 mg sub.: 9.54 ml 0.02 N $AgNO_3$. Found %: N 13.71; Cl 17.34. $C_{10}H_5ON_2Cl$. Calculated %: N 13.69; Cl 17.33.

4-Chloronaphthofurazan. It was prepared analogously to the 3-chloro derivative from 2.72 g (0.0094 mole) of the sodium salt of naphthofurazan-4-sulfonic acid, isolated in the fused state; yield 1.76 g (91.7%), m.p. 92-94°.

It consisted of colorless needles (from alcohol), m.p. 96.8-97.1°; quite soluble in alcohol and acetic acid.

2.942 mg sub.: 0.377 ml N_2 (28°, 719 mm). 35.458 mg sub.: 8.777 ml 0.02 N $AgNO_3$. Found %: N 13.72; Cl 17.55. $C_{10}H_5ON_2Cl$. Calculated %: N 13.69; Cl 17.33.

SUMMARY

1. Contrary to the data of Green and Rowe, by nitrating 1,2-naphtho-(3',4')-furazan in sulfuric acid in the cold with a 40% excess of nitric acid, not only the mononitro derivative, but also the dinitro derivative was obtained.

2. During the mononitration of 1,2-naphtho-(3',4')-furazan, there is formed not one nitrocompound with the nitro group in position 5- or position 8-, as Green and Rowe asserted, but two compounds: 5-nitro- and 7-nitro-1,2-naphtho-(3',4')-furazan.

3. The direct chlorination of 1,2-naphtho-(3',4')-furazan in the presence of iron leads to 3-chloro-1,2-naphtho-(3',4')-furazan.

4. The corresponding 3-chloro- and 4-chloro-1,2-naphtho-(3',4')-furazans are formed by the action of potassium chlorate on 1,2-naphtho-(3',4')-furazan-3- and 4-sulfonic acid in a hydrochloric acid medium.

5. 1,2-Naphtho-(3',4')-furazan-5-sulfonic acid is formed by the action of hydroxylamine on 1-nitroso-2-naphthol-5-sulfonic acid in alkaline medium.

6. Nitronaphthofurazans are converted by reduction into aminonaphthofurazans.

7. 5-Chloro-, 5-hydroxy-1,2-naphtho-(3',4')-furazans and 1,2-naphtho-(3',4')-furazan-5-sulfonic acid are obtained via the diazo compound from 5-amino-1,2-naphtho-(3',4')-furazan, while 7-chloro- and 7-hydroxy-1,2-naphtho-(3',4')-furazans are obtained from 7-amino-1,2-naphtho-(3',4')-furazan.

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* See Consultants Bureau Translation, page 2127.

THE DEVELOPMENT OF THE THEORY OF CHEMICAL STRUCTURE IN THE WORKS OF V. V. MARKOVNIKOV

(On the 50th Anniversary of His Death)

V. V. Razumovsky

The outstanding Russian chemist, Vladimir Vasilyevich Markovnikov, was born on December 10 (23), 1838, in the village of Chernorechye, not far from Nizhny Novgorod (now Gorky). He received his secondary education in the Nizhegorod Institute for the Nobility. In 1856 Vladimir Vasilyevich entered Kazan University in the Commercial Section of the Faculty of Law. The commercial section gave a broad training both in general knowledge and in natural science.

Chemistry was taught in the commercial section of Kazan University by A.M. Butlerov and technology by M. Ya. Kittary. V. V. Markovnikov developed a special interest in chemistry. While a student of the third course, V. V. Markovnikov wrote down and reproduced by lithography the course of lectures delivered on organic chemistry by A.M. Butlerov in the 1859/60 academic year.

In 1862 he delivered a course of lectures on inorganic chemistry, deputising for the indisposed Butlerov, and in 1863 he delivered a course on analytical chemistry.

In 1863 Vladimir Vasilyevich passed his degree examination and in 1865 he defended his doctoral dissertation on "The isomerism of organic compounds" which played an important part in the development of the theory of chemical structure.

In 1865 Markovnikov went abroad to work in the laboratories of the greatest German chemists of last century — Erlenmeyer in Heidelberg, Kolbe in Leipzig and Baeyer in Berlin. While abroad, he continued to follow the work of his teacher on the theory of chemical structure. V. V. Markovnikov wrote to A. M. Butlerov from Berlin:

"Your researches, as formerly, are very interesting and are evidently moving unerringly toward a solution of the problems you have set yourself" [1]. He was keenly interested in the political life of Germany, about which he wrote as follows in the same letter:

"I should like to go to Switzerland but the direct road is not yet free. The Germans continue to fight but probably not for much longer. After the peace between Prussia and Austria, which will very soon be concluded, it will only remain for the young Germans to submit to the will of Bismarck. The Germans in this town were so carried away by their victories that reasoned discussion with them was out of the question. They imagine that Prussia can now do what she likes and that nobody is in a position to say them nay because nobody else possesses needle guns. . I did not fail to tell my fellow students that they were stupid" [1].

In 1867 Markovnikov returned to Kazan on the occasion of his selection by the University Council as docent of the chair of chemistry. V. V. Markovnikov wrote as follows to Butlerov from Leningrad on March 11, 1867:

"I am very thankful to you, dearest Aleksandr Mikhailovich, for the notification of the successful outcome of my work. I completely lost patience while waiting for your letter and was about to send you a telegram. I myself expected more adverse votes than I received, and for the favorable outcome, as in general for my appointment, I have only you to thank. I think it would be out of place to amplify my expressions of thanks because, of course, you were actuated in this matter principally not by any personal disposition toward myself but by your sense of public duty in relation to the university. It only remains for me to justify the expectations of yourself and the faculty. That the desire to do so is strong, I give you my word of honor — my doubt is as to the adequacy of my talents ... In a few days I shall send a petition to the Ministry for a deferment until October. It is still necessary for me to spend the whole of the summer semester here and to visit Paris. Apart from that I should very much like to attend the congress of chemists" [2].

At the end of December 1867 and the start of January 1868, V. V. Markovnikov took an active part in the work of the first congress of Russian naturalists and doctors in Petersburg under the auspices of the Russian Chemical Society.

Describing the congress to Butlerov, who was abroad on a mission, Markovnikov wrote:

"On the whole the congress could not have been more successful. Everybody appears to be satisfied. Among the papers presented at the sittings, those of Engelhardt and Beilstein were particularly interesting, the former because of its expression of divergence from Kekule's theory...Beilstein dealt with the chlorination of toluene. His method enables gradual substitution of the whole of the hydrogen, either in the methyl or in the phenyl. At will one can also substitute the hydrogen either in the one radical or in the other. He also found that with water chlorotoluene reacts to give benzaldehyde which is already being produced in Berlin by this method from toluene.

"For chemists the congress was useful if only because of the unanimous desire to found a chemical society in Petersburg and the ministry has already promised to authorize it. It is planned to publish the work of Russian chemists as soon as material is communicated...Six of us were at the congress and Kazan in general created an effect! We constantly received thanks for our active participation, and even at the farewell dinner the chairman, after toasting all the universities together, proposed a special one for Kazan University" [3].

In 1868 A. M. Butlerov was chosen as full Professor of the Chair of organic chemistry at Petersburg University. After Butlerov had been transferred to Petersburg, the chair of chemistry was occupied by V.V. Markovnikov. At this period Markovnikov was working out the theory of the mutual influence of atoms in molecules. In 1869 Markovnikov defended his celebrated doctoral dissertation on "Data on the question of the mutual influence of atoms in chemical compounds". In response to the suggestion that the dissertation should be translated into German, Markovnikov declared:

"If the ideas here expounded are of interest, those wishing to do so may make use of this Russian paper" [4].

The pioneer scientist and patriot V.V. Markovnikov all his life defended the priority of Russian science and carried on a fight against the printing of the papers of Russian chemists in foreign languages.

Not only did he himself publish all his papers originally in Russian, but he urged all Russian scientists to do the same. V.V. Markovnikov also put this problem before Butlerov who at that time headed the Petersburg school of chemists:

"Tell me please why all the Petersburg chemists have begun to publish again their work in foreign journals even before they are published in the Russian language? What then is the purpose of our society and journal? I find this completely tactless, and if it continues I shall leave the society" [5].

Markovnikov's patriotism and his active fight for the honor and dignity of Russian science provoked the hostility of scientific opponents, and principally of members of foreign academies. Subsequently this was also clearly manifested in the Academy itself.

The conversation of Markovnikov with the academician Yu. F. Fritsche was characteristic:

"Nothing of any interest was of course to be expected from a meeting with Fritsche. Suddenly he began a conversation about the reproaches made against the Academy for bringing out its bulletin in German, and he naturally defended this policy" [6].

In 1869 Markovnikov was elected extraordinary professor of Kazan University and in 1870 he became ordinary professor. At the same period A.M. Butlerov was elected to the Academy of Sciences and Markovnikov, in a letter of congratulation, expounded his unusual ideas about the value of lectures in a higher educational course:

" However dull lectures may sometimes appear, they have the advantage of allowing one's own ideas to be put forward. This opportunity is not open to any of the academic staff who are not professors because in papers it is inconvenient to say all that one might say at lectures. However small my audience, I can always try out my ideas on them" [7].

In October, 1871, Markovnikov resigned his professorship at Kazan University as a mark of protest against the illegal dismissal of the outstanding Russian scientist and public-spirited worker, the professor of anatomy P. F. Lesgaft.

On this matter Markovnikov wrote as follows in a letter to Butlerov on October 25, 1871: "...You understand that the conditions existing at Kazan University at the present time make it impossible to remain there, and that is why I am compelled to ask you for help in getting away from Kazan. We are definitely convinced that we are in danger because we are surrounded by a network of the darkest and most inadmissible intrigues whose first victim was Lesgaft. The persons known to you are not scrupulous in their methods even if these should lead to unrest among the students..." [8].

At the end of 1871 Vladimir Vasilyevich was chosen as ordinary professor of chemistry of the Novorossiysk University in Odessa. However he spent the 1872/73 academic year in Odessa. At this time, the rectorate of Moscow University, wishing to raise the teaching of chemistry to a high level, invited D. I. Mendeleev to fill the chair of Chemistry. D. I. Mendeleev was closely attached to Petersburg and was compelled "to refuse in honor to give up his work at the oldest Russian university" [9]. In his letter of September 28, 1871 to the dean of the physico-mathematical faculty of Moscow University (A.Yu. Davydov), Mendeleev indicated Markovnikov as the most meritorious candidate for the chair of chemistry. In the summer of 1872 Markovnikov was invited by Davydov to transfer to Moscow University. In 1873 the Council of Moscow University chose Markovnikov as ordinary professor of chemistry.

"During the Science Congress in Moscow in 1869" — we read in Markovnikov's autobiography — "the status of chemistry at this university made an extremely poor impression on all Russian chemists. It was generally considered that chemistry was absent from Moscow" [10].

At Moscow University Markovnikov undertook the enormous task (extending over many years) of organizing and equipping the chemical laboratory and of constructing a new and large laboratory. The number of natural science students wishing to take chemistry under the guidance of Markovnikov steadily increased from year to year. From Markovnikov's laboratory began to be published researches in considerably greater number than from any other Russian chemical laboratory.

At Moscow University Markovnikov founded the most important school of Russian chemists, as represented by: N. Ya. Demyanov, I.A. Kablukov, N. M. Kizhner, M.I. Konovalov, A.E. Chichibabin, A.M. Berkengeim, N.I. Kursanov, Yu. V. Lermontova, V. N. Ogloblin, P.P. Orlov, A.N. Reformatsky, A.P. Sabaneev, A. N. Shchukarev and A.A. Yakovkin.

Vladimir Vasilyevich occupied the chair of analytical and organic chemistry of Moscow University for 20 years (1873-1893). In 1893/1894 the chair was occupied by Professor N.D. Zelinsky.

Markovnikov did not, however, leave Moscow University but continued to work there on a restricted scale right to his end on February 11, 1904. In the last decade of his activity at Moscow University he carried out scientific research and guided several students and co-workers.

A vivid picture of the scientific activity of Markovnikov at Moscow University was drawn by K.A. Timiryazev when commemorating the fortieth year of the scientific activity of the great Russian chemist:

"What chemistry was at Moscow University before you and what it has become, thanks to you, is evident to us. It was certainly no coincidence that in the same period prior to you two scientific papers were published from this laboratory, while in your time the number was two hundred. Nor is it fortuitous that with your arrival in Moscow and the almost simultaneous arrival of A.G. Stoletov as professor of physics, the entire destiny of the natural science section of the mathematical faculty was changed. The number of students which had steadily fallen from 17 to 1 in the forth course, suddenly began to increase to 100 and then to 600-700" [11].

In Moscow University Markovnikov started and completed his classical investigations of Russian petroleum and made the most valuable contributions toward the development of knowledge of the reciprocal influence of atoms.

The 20 years in which Markovnikov studied the chemical nature of Russian petroleum opened up the widest perspectives for the development of the science of petroleum and for the chemical industry. Prior to the investigations of Markovnikov only a few facts were known about the composition of Russian (Caucasian) petroleum and some erroneous statements had been published.

In the laboratory of Moscow University, Markovnikov and his students carried out systematic investigations of the composition of Caucasian petroleums, of the chemical and physical properties of individual fractions: elementary composition, ash content, acidity, optical activity, refractive index and coefficient of expansion. By repeated fractional distillations Markovnikov effected resolution of the fractions of Caucasian petroleums and isolated their narrow cuts. Markovnikov's investigations showed for the first time that the chemical nature of Russian (Caucasian) petroleum was quite different from that of American (Pennsylvanian) oil. He discovered that the main components of Caucasian petroleum were naphthenes (cycloparaffins). The individual hydrocarbons isolated by Markovnikov from Caucasian petroleum proved to be derivatives of cyclohexane and cyclopentane [12].

Markovnikov widened the scope of his petroleum researches by synthesizing numerous naphthenes and their derivatives (naphthenic acids) with the aim of studying the structure of the hydrocarbons of Caucasian petroleum. In his laboratory he synthesized five-, six- and seven-membered polymethylene hydrocarbons.

1,3-Cyclobutanedicarboxylic acid, synthesized for the first time by Markovnikov and G.A. Krestovnikov (1880), was the first synthesis of a carbocyclic system with four carbon atoms in the history of organic chemistry. This investigation of Markovnikov refuted the then widespread idea of the impossibility of existence of four-membered carbon rings. Later (1893) Markovnikov obtained cycloheptane in his laboratory and thus disproved Baeyer's strain theory which postulated the possibility of existence of only five- and six-membered cyclic compounds [13].

The investigations of suberone (cycloheptanone) and its derivatives, which also led the scientist to the discovery of the seven-membered carbon ring, were actually the climax of his experimental activity in chemistry.

Markovnikov approached the study of the dynamics of polymethylene rings and their intramolecular rearrangements on the basis of the theory of the mutual influence of atoms. He studied the isomeric transformations of cycloheptane and cyclohexane hydrocarbons and their derivatives [14]. His study of the molecular rearrangements of polymethylene hydrocarbons led Markovnikov to the notable discovery of the contraction of carbon rings. He observed this phenomenon for the first time in the conversion of a seven-membered into a six-membered ring.

On the suggestion of Markovnikov, his pupil N.M. Kizhner carried out the hydrogenation of benzene and made the important observation of the transformation of benzene into methylcyclopentane [15].

Another pupil, N. Ya. Demyanov, continued Markovnikov's work in the field of the molecular dynamics of cyclic systems and established the fundamental laws of expansion and contraction of polymethylene rings.

In a study of the stability of cyclopentane hydrocarbons, Markovnikov established that the five-membered ring is ruptured under the action of hydriodic acid with formation of paraffins [16].

These discoveries and investigations of Markovnikov predetermined all later investigations and achievments in the chemistry and technology of petroleum down to the present day.

Markovnikov also discovered aromatic hydrocarbons (benzene, toluene, pseudocumene, diethylbenzene, isoamylbenzene, etc.) in Caucasian petroleum.

"My researches with petroleum" — he writes — "are making progress and interesting things are coming to light. It appears that petroleum contains an extraordinary diversity of aromatic hydrocarbons, representing up to 20% of the oil after purification from oxygenated compounds. But each fraction contains very little, and that is why they are very difficult to separate. However, at the next meeting there will probably be something to report" [17].

Markovnikov established the genetic relation between naphthenes and aromatic and aliphatic ("fatty") compounds and discovered their structures and their characteristic chemical reactions [18].

The methods used by V. V. Markovnikov for chemical working-up of the narrow fractions of petroleum (nitration, sulfonation, oxidation, chlorination, iodination, bromination and sulfur-dehydrogenation) enabled him and his pupils to obtain numerous derivatives of petroleum hydrocarbons of enormous value for our national economy and modern chemical industry.

Markovnikov left the study of petroleum to take up the investigation of other natural products.

He said: "I am entirely unable to see anything opprobrious in a Russian professor of chemistry carrying out applied research" [19].

Together with A.N. Reformatsky he studied the composition of rose oil. This investigation brought out more prominently the link between napthenes and terpenes. Markovnikov examined Turkestan manna and isolated a sugar from it [20]. He demonstrated that Turkestan manna is melezitose. A thorough investigation of melezitose was carried out in Markovnikov's laboratory in Moscow University by A.V. Alekhin.

The scientific work of V.V. Markovnikov, combining theory with practice, dominated the Russian conception of chemistry.

In 1884 Markovnikov formed a chemical committee in the physical division of the Society of Naturalists, Anthropologists and Ethnographists, which in 6 years was reorganized into the chemical division of the society. From 1884 to 1904 Markovnikov headed in succession the chemical committee and the chemical division of the Society of Naturalists, which constituted the scientific association of Moscow chemists.

With full reason Markovnikov observed:

"In short I wish to take the liberty to say that only my chemical researches, so to speak, originated in Moscow, as I previously mentioned in my address this year to the chemical division on the occasion of my refusal of the chairmanship" [21].

The Tsarist regime not only did not value the highly fruitful activity of V.V. Markovnikov in Moscow University, but even deprived him of his chair.

With bitterness and anger Markovnikov wrote:

"And what do they tell me in gratitude for all that I have done: Get out of here! You are not needed!" I listen for sympathy from chemists. But does anything happen? On my word as a chemist they put a cross, although I could still work on with profit. Not only am I insulted but also Russian science..." [22].

The great services of V. V. Markovnikov to Russian science enabled Academician A.M. Butlerov, jointly with Academicians N.N. Koksharov and V.G. Imshenetsky on November 9, 1882 to propose his candidature as a corresponding member of the Academy of Sciences in the Chemical Division.

In his presentation Butlerov wrote:

"In his researches Markovnikov has been mainly occupied with phenomena of isomerism of organic substances and with the question of the mutual influence of atoms in chemical compounds. His publications on the first theme deal with: the bromide of allyl alcohol; isobutyric acid, which Markovnikov obtained for the first time, independently of Erlenmeyer - the identity of "acetonic" acid with one of the hydroxybutyric acids; and the isomerism of pyrotartaric acid. All these investigations had great value in clarifying the chemical structure of the compounds mentioned as well as for the theory of structure itself. In the second group of researches we mention in particular those on aliphatic hydroxy acids which greatly aided the elucidation of the laws involved in the substitution of the hydrogen of aliphatic organic compounds and solution of the problem of the order in which the hydrocarbon groups in a molecule are influenced by radicals. Nor has Markovnikov shunned the applications of our science. Thus he participated in the organization of disinfection on the battlefield during the last Eastern War; some of his papers deal with various problems of industry; for some time, in collaboration with one of his pupils (Ogloblin), he has been investigating Caucasian petroleum and has already published many results" [23].

On November 13, 1882 the permanent secretary of the Academy of Sciences K.S. Veselovsky notified Academician A.M. Butlerov that "the agreement of the President to this had not been obtained" [24].

Exactly a year later, A.M. Butlerov with the permission of the President again proposed V.V. Markovnikov as corresponding member in chemistry and particularly stressed the value of his candidate's work on the chemistry of petroleum:

"The investigations of Professor Markovnikov on petroleum, carried out with one of his pupils (Ogloblin), have now been published in detail in an exceptionally long paper and have been acknowledged by the University as worthy of the award of the Ilyenkov Prize" [25].

In connection with his presentation in the Academy of Sciences, Markovnikov wrote to A.M. Butlerov:

"I thank you, dear Aleksandr Mikhailovich and others, for your compliments. I shall naturally not refuse the honor if the Academy elects me a corresponding member and I shall conscientiously try to fulfill my obligations".

"It seems to me, however, that I shall not be granted this honor. They will naturally ask Beilstein for his opinion, and I have not the slightest reason to expect a favorable testimonial from him, judging by his attitude toward me during the exhibition, although outwardly our relations were good. Probably he will recommend the more neutral Zaitsev. By this choice the Academy will escape the embarrassment of being in conflict with you. By the way, about Friedrich (F.F. Beilstein — author). Should I not send to the next meeting of the society several results of work with petroleum which contradict his conclusions? What do you think?" [26].

The reactionary majority of the Academy voted against the great Russian scientist and public worker, as well as against Butlerov's other candidates — A.M. Zaitsev and N.A. Menshutkin — and in their place they elected second-rate German Scientists and even foreign subjects.

This same reactionary majority of the Academy also blackballed the first of Butlerov's candidates as active member of the Russian Academy of Sciences — the great Mendeleev.

In the sixties of the 19th century the central problem of organic chemistry was that of isomerism. Round the problem of isomerism in those years raged the battle for the atomic-molecular theory of the structure of substances, the battle for materialism in chemistry.

Gerrard's mechanistic theory of types proved completely incapable of explaining the numerous phenomena of isomerism in organic chemistry. Gerrard claimed that experiment enabled us only to distinguish past and future substances, but not those actually existing. The irrational views of Gerrard led him to completely reject the concept of the internal structure of a substance, the structure of isomers of molecules.

V. V. Markovnikov in his magisteral dissertation exposed the fundamental errors of Gerrard's theory of types in elucidating the nature of molecules and their isomerism: "Assuming the chemical particle to be an indivisible whole, Gerrard also rejected the possibility of evaluating the internal arrangement of atoms in them with the help of chemical transformations alone...In his opinion, chemistry may study a substance only in the past and future, but the present belongs to physics, for which chemical reactions serve only as an auxiliary in comparing the concepts of the structure of materials. It is agreed that such an opinion, postulated as a basis for the whole of science, could not be fruitful for elucidation of the cause of isomerism" [27].

In this connection, Vladimir Vasilyevich acknowledges the great scientific services of Gerrard in the development and experimental founding of the ideas of Avogadro and Ampere and in the defining of the fundamental concepts of chemistry: "atom", "molecule", "equivalent".

In the course of his work on the development of the theory of chemical structure, Markovnikov wrote that "...the definitions of isomerism and metamerism given by Butlerov do not clearly express the significance of the examples adduced. The following definition will be in perfect accord with the theory of chemical structure. Isomers are substances whose radicals, with identical number of carbon equivalents directly linked with one another, contain the same number of other equivalents differently arranged in relation to the carbon" [27].

Markovnikov's definition of isomerism was later adopted by Butlerov in his classic work —"Introduction to the Complete Study of Organic Chemistry", [28].

Markovnikov's dissertation was permeated by the idea that only the theory of chemical structure can truly explain the cause of isomerism.

Markovnikov wrote: "By applying the concept of chemical structure we can explain the difference in the majority of known cases of isomerism. It is evident that the more complex is a substance, the greater the possibilities for a different grouping of the elements, and consequently also the number of isomers must increase" [27].

Markovnikov brings forward many examples to show that isomerism is the inevitable consequence of a specific order of the chemical bond in atoms and molecules. Referring to the isomerism of saturated alcohols, he established that "the number of isomers increases not only with increasing amount of carbon in a radical, but also with increasing number of non-carbon radicals" [27]. Markovnikov also quite specifically indicates the influence of external conditions on the direction of isomeric transformations of molecules: "It is likewise not improbable that an influence is exerted by the temperature, the reaction energy, and other conditions, as yet little known to us, so that from one and the same alcohol under various conditions we can obtain different isomeric hydrocarbons" [27]. In the search for isomers of molecules, Markovnikov resorted to a profound study of the structure of substances, to an exhaustive examination of the by-products of reactions: "...the large number of so-called by-products has been investigated only superficially. But in part of them is contained the whole diversity of transformed isomeric substances; sometimes only an exhaustive study of all the products formed in identical conditions can give good assistance in establishing whether we are dealing with identical or isomeric substances" [27].

In the 18th century the sole method of study of the composition of a substance was analysis. According to the chemistry of his day, Lavoisier was defined as an analytical chemist. The successes of the analytical method in the study of substances led to the definition of an element as the limit of chemical analysis. In the forties of the 19th century Gerrard proposed the method of double decomposition for the study of the composition of a substance. He assumed that the greater the number of double decompositions that can be expressed by the formula of a substance, the more rational is that formula. As early as the forties of the 18th century (1749), however, Lomonosov had embarked on the study of the composition of substances from a deeply materialistic angle. For the understanding of the nature of a substance he proposed to combine analysis with synthesis. Lomonosov pointed out: "... in chemistry synthesis is often more trustworthy than analysis, and it even suffices in itself to identify components" [29]. By underlining the unity of analysis and synthesis in the understanding of the nature of a substance. Lomonosov discovered new analytical techniques; "...but in association with synthesis analysis endows it with much weight, and itself gains much thereby" [29]. The significance and the role of the experimental method indicated by Lomonosov for the study of composition and structure was fully revealed by materialistic dialectics.

"Chemistry in which the form of the investigation predominates is analysis" — wrote Engels — "but it is worthless without its antithesis (synthesis)" [30].

Summing up a century of the experimental study of the composition and structure of molecules by the chemical method, Butlerov stated:

"Conclusions about the chemical structure of a substance can best be reached in all probability on the basis of study of the methods of their synthetic formation..." [31].

Developing the synthetic trend in chemistry, V. V. Markovnikov carried out an investigation of the synthesis of organic acids. He was the first to synthesize isobutyric acid, whose existence he predicted on the basis of the theory of structure. His investigation demonstrated the fallacy of Erlenmeyer's hypothesis of the structure of butyric acid and its isomer, both of which he regarded as identical.

Markovnikov wrote: "Isobutyric acid is the first example of isomerism in the monobasic fatty acid series" [27].

Markovnikov's researches resolved the problems of the structure and isomerism of hydroxybutyric and bromobutyric acids about which ideas were very confused at that time. Studies in this field by eminent foreign chemists (Wurtz, Frankland and Duppa, Wislicenus and others) were only correctly interpreted after Markovnikov had applied to them the theory of chemical structure. Subsequently Markovnikov studied the structure and isomerism of bromo- and hydroxyisovaleric, hydroxyisocaprylic and pyrotartaric acids. He also studied the structure of allyl bromide and the isomerism of oxygen-containing derivatives of propane in order to demonstrate the accuracy of the predictions of the theory of chemical structure [33].

From a letter by Markovnikov to Butlerov from Heidelberg (1865) we learn that the investigation of the isomerism of valeric acid was among the plans of the young scientist.

The extent to which such projects were among the scientific plans of Markovnikov is evident from the fact that the study carried out by A. M. Butlerov in 1872 of the isomerism of valeric acid led him to the synthesis of a new isomer of valeric acid — trimethylacetic acid.

Problems of structure and isomerism of acids and their derivatives predominantly engaged Markovnikov throughout the whole of his scientific career. Thus in 1874 he wrote as follows from Moscow to Butlerov in Petersburg:

"Would you ask Menshutkin whether he retained in the editorial office my paper on the oxidation of hydroxybutyric acid which I sent from Kazan and did not publish on your advice.

"Now, in view of the appearance of the paper of Popov and Lei on the same topic, it acquires some value, for the facts there described are true. I did not keep a copy and I should like you to send it to me if it has been kept. After suitable modification in the light of the present situation, I intend to publish it" [34].

And in 1875 in the pages of the Journal of the Russion Chemical Society appeared Markovnikov's paper on the products of oxidation of α-hydroxybutyric acid [35].

Markovnikov's discovery of the isomerism of the organic acids, as predicted by the theory of structure, showed that chemical structure provides the key to the scientific clarification of the phenomena of isomerism.

These investigations of Markovnikov played an important part in the strengthening and recognition of the theory of chemical structure.

In Germany Markovnikov was a protagonist of the ideas of the theory of chemical structure in opposition to the views of German chemists. In Heidelberg Markovnikov had fierce debates with Erlenmeyer on the principles of the theory of chemical structure.

Erlenmeyer, Kekule and Kolbe were for many years protagonists of the hypothesis of different units of affinity in atoms. On the basis of this hypothesis the German chemists made serious mistakes in connection with problems of the isomerism of alcohols, ketones and other organic compounds. Kekule, for instance, inferred the existence of three propyl alcohols on the basis of the hypothesis of difference in units of affinity. Kolbe postulated the existence of two isomers of methylpropyl ketone.

As early as 1862 Butlerov abandoned the hypothesis of difference of units of affinity in polyvalent atoms due to his pupil's views on the reciprocal influence of atoms in a molecule.

Butlerov wrote: "Not only here and now, when speaking of the difference of units of affinity, must we draw attention to the factor (see paper on chemical structure) which influences the nature of the units of affinity, of the nature of bonds which link other units; and it is even necessary to add that the difference may be conditioned by this influence" [36].

Concerning the views of Erlenmeyer on the difference of units of affinity, Markovnikov wrote to Butlerov:

"For the present he has abandoned the difference of units of affinity, but once he said to me: 'Wait a bit'. I am now keeping quiet about this, but I am working and wish to demonstrate facts. Kolbe is doing likewise.' I answered that then I would be the first to admit the inadequacy of the theory of chemical structure but at the same time I perhaps could not accept the difference of affinity because other causes may also come into play" [37].

The controversies of Markovnikov with Erlenmeyer gradually extended over the most fundamental problems of chemical structure. Markovnikov comments at length on these debates in a letter to Butlerov from Heldelberg on April 12, 1866:

"Disputes arose apropos of the "doctrine of constitution" with which Erlenmeyer concluded his lectures.. After Kolbe had spoken, he reminded us of his communication on the isomerism of glycols which I had not yet read and therefore did not know about the errors which it contained. But in the evening Eremeich (this was what Russian chemists in Germany called Erlenmeyer – author) told me how some chemists had reproached him for publishing your "Prognoses" in his journal; whereupon I asked him why nobody made any comment when he published Kolbe's "Prognoses".

"...I told you that recently we conversed about chemists and your achievments; he then made nearly the same comment as Heinz (in Annalen) and added that they would be far more appreciated if you would completely abandon type formulas. About such type formulas, as you know very well, Butlerov uses brackets and other type attributes not in the sense of types. I know that, but others do not understand this distinction and therefore obstinately cling to types under the impression that they express the same thing. Tell Butlerov that with these people it is necessary to pull out the tongue and smear it with porridge and not to let go, otherwise everything runs off, but to push it again into the mouth. Only then are they able to swallow.

"And after this he says at the lecture that you make use of type formulas." [38].

In Berlin Markovnikov became acquainted with the trend of the scientific investigations of Adolf Baeyer and his laboratory. He was specially interested in Baeyer's work on the structure and synthesis of indigo and in his method of distillation with zinc dust [39].

During Markovnikov's stay in Herman Kolbe's laboratory there was continuous discussion about problems of the theory of chemical structure. Kolbe did not appreciate that a molecule is qualitatively a specific entity and that was why he could not find a solution of the problem of its internal structure. That was why he sharply criticized the ideas about the bond of atoms in a molecule – ideas first put forward by Lomonosov. As early as 1738-1741 M. V. Lomonosov, in developing his ideas about the linking of atoms, arrived at the conclusion that molecules with differing properties may be obtained by different linkings of the same atoms [40]. Lomonosov's atomic-molecular doctrine of the possibility of formation of molecules by linking of identical atoms was disputed more than 60 years later by Dalton who was of the opinion that "complex" atoms can be obtained only by linking of different atoms. Naturally, it is impossible to credit Kekule with the priority for the idea of the linking of identical atoms, an idea enunciated by Kekule 119 years after Lomonosov.

By rejecting the principle of the linking of atoms in a molecule, Kolbe rejected the main scientific principle of the theory of structure of organic compounds.

Vladimir Vasilyevich makes the following comments about Kolbe's theoretical views:

"Kolbe is remarkably obstinate in retaining his previous views and evidently considered it entirely superfluous to read any criticisms of himself. As a worker in his laboratory my own position was somewhat delicate during these debates. But the logic of events was on my side. The erroneous conclusions of Kolbe largely stemmed from the fact that in his formulas he made use of the old atomic weight of oxygen, and no matter how much I urged him to try to express his ideas with the double bond of oxygen, he refused, believing that it was all the same. Kolbe certainly attached little importance to my objections and obstinately held to his views in face of the facts...When the professor went off, the more daring of his assistants ventured to say that he is wrong. This was flattering to my young self-esteem but I could not help feeling that I owed my victory to my Kazan teacher, and to this I drew the attention of my German comrades" [41].

The most important stage in the development of the theory of chemical structure and in the solution of the problem of isomerism was Butlerov's classic paper on the "Various methods of clarifying some cases of isomerism" which was published in 1863. The author naturally wished to bring the paper to the attention of prominent foreign chemists, in particular Kolbe. Markovnikov wrote, however, to Butlerov:

"He (Kolbe – author) is terribly obstinate and nothing at all will convince him that some of his ideas not only lack all factual basis but are even opposed to the facts. For example, the different methyls in ethane. Due to this I am trying to avoid any arguments on this topic" [42].

In his polemic with Kolbe on the fundamental problems of theoretical chemistry, Markovnikov discussed only the essential problems of science, strictly keeping to facts, just as he expected others to do. He did not agree with Butlerov in his unprovoked attacks on Kolbe, nor with the character of the criticism of A.M. Popov, whose investigations of the oxidation of ketones had proved the fallacy of Kolbe's ideas on isomerism .

In a letter from Heidelberg dated April 12, 1866, Markovnikov frankly states his opinion to Butlerov:

"I now wish to refer to your paper in the Bulletin and, in particular, to the paper by Popov which you certainly wrote. Frankly I must say that I was not pleased with your attacks on Kolbe, because you will thus put a weapon in Kekule's hands; also Popov's paper was too sharp. Such a tone is out of place for a young chemist in relation to a person deserving, in spite of all his mistakes, full respect: it is particularly out of place in relation to Kolbe who would never permit himself to treat anybody so high-handedly as Kekule does. I hope you will excuse me for the strictness of my statement because I do this in the interests of the Kazan laboratory and, consequently, in your own interests. I even think that for the time you should refrain from polemics and stand on the facts" [43].

Markovnikov urgently advised Butlerov to visit Germany for the Naturalists' Congress in order to acquaint a wide circle of German chemists with new researches on the theory of chemical structure. In 1867 the physico-mathematical faculty of Kazan University proposed that Butlerov should go abroad in order "to give Mr. Butlerov the opportunity of personally explaining to foreign chemists his claim to have taken the main part in the development of the trend now being followed by chemistry" [44].

Apropos of this, Markovnikov wrote as follows from Heidelberg to Butlerov in Kazan:

"I congratulate you on your leave of absence and hope to meet you in Leipzig. You must come to Germany in July if you wish to find the professors at their work, because in August everybody goes away to various places. Yesterday Kolbe told me that he would be very pleased to meet you but he will be staying in Leipzig only until the beginning of August. Nothing has yet been heard about the Naturalists' Congress and possibly there will be no congress at all this year" [45].

In 1864 Butlerov summarized his investigations on the creation of the theoretical bases of organic chemistry and published a substantial work on "Introduction to the Complete Study of Organic Chemistry". This classic book was the first in the history of world chemistry in which the theory of structure permeated the whole of organic chemistry. Markovnikov made these noteworthy comments about Butlerov's book:

"We certainly cannot help feeling proud that a work has been published in the Russian language which for the first time presents a detailed exposition of a doctrine which over a period of a quarter of a century has continued to render such dazzling services to science. We must be particularly grateful to A.M. Butlerov because, knowing what a limited circle of readers there is for his book in Russia, he did not follow the example of many Russian scientists by first publishing important work in foreign languages" [46].

However Markovnikov conscientiously examined the work of his teacher in the original and made a number of critical comments in regard to some chapters and sections.

With his inherent scientific conscientiousness and the bluntness of the Russian, he told Butlerov what he thought about the "Introduction":

"I have read a part of the "Introduction" and it seemed to me that some of the sections were too compressed, for example the historical outline of the theory; so that to anyone wishing to familiarize himself with this aspect of the history of chemistry it would be impossible to keep it in mind from your outline unless he nearly learned it by heart" [47].

Markovnikov advised Butlerov:

"...It would be desirable for a part of the theoretical considerations on the existence of different new substances to be replaced by a more detailed enumeration of the compounds in this group and their diverse transformations...It also seems to me that the inclusion of amino acids and certain others in the section on nitrogen-containing compounds, although in accordance with your adopted classification, is inconsistent with their natural connection with the halogen and hydroxy acids" [48].

In defending the interests of Russian science, Markovnikov fought energetically to establish the priority of A.M. Butlerov in the creation of the theory of chemical structure not only by word but with the pen. One of the elements of this struggle was his resolute participation in the translation of Butlerov's "Introduction" into German. Vladimir Vasilyevich considered it necessary to warn his teacher:

"Your hopes for help from Beilstein and Erlenmeyer are likely to be disappointed. Each of them is busy with his own work and the second in particular has little free time. He is bringing out a handbook of organic chemistry" [49].

In 1867 the German edition of "Introduction to the complete study of organic chemistry" was published in Leipzig under the closest participation of Markovnikov. This gave foreign chemists the opportunity of becoming well acquainted with Butlerov's theory of chemical structure as applied to all classes and groups of organic compounds.

Markovnikov wrote: "In the interests of science and my teacher, I cannot fail to rejoice at the appearance of this translation. Having lived two years in Germany and become acquainted with many chemists, I am convinced that such a publication was needed".

In the pages of his magisteral dissertation on the "Isomerism of organic compounds", Markovnikov demonstrated for the first time the utter inadmissibility of Kekule's pretensions to priority in the creation of the theory of chemical structure which were afterwards echoed by some foreign chemists. In this work Markovnikov wrote:

"While being an ardent supporter of the theory of types, Kekule has recently become an adherent of the same theory which was developed in detail by Butlerov under the name of chemical structure. But unfortunately we do not find that acknowledgment of priority which was rightly to be expected from Kekule; it appears that the idea itself is still not sufficiently clearly appreciated". [27].

In his researches Kekule did indeed adhere strictly to the theory of types. While putting forward the concepts of valence of elements, of the linking of atoms and of the chemical constitution of compounds, Kekule simultaneously expressed his belief in the conditionality, subjectivity and arbitrariness of the concepts of atoms, molecules and structure (constitution) of chemical compounds. Generalizing the experimental material which did not fit into the framework of Gerrard's theory of types, Kekule began to develop the concepts of mixed and complex types. Following Gerrard, Kekule asserted that "rational" formulas describe only the chemical transformations of a substance and are incapable of reflecting its internal structure.

Markovnikov emphasizes that: "The importance which Kekule attaches to types is already evident from the fact that each rational formula in his papers is accompanied by the corresponding type. This desire to permanently class all substances in specific types compels him to attribute to them more significance than they actually deserve and to thereby relegate valence to a secondary place" [27].

In making a systematic analysis of the theoretical studies of Kekule and in particular of his textbook of organic chemistry, Vladimir Vasilyevich remarks:

"His rational formulas are nothing else than transformation formulas (Umsetzungsformeln) and not constitutional formulas. That is why he often thinks several formulas can be given for one substance, these formulas serving to indicate different analogies..." Markovnikov makes this final comment at the end of his critical survey: "The student reaches a faulty conclusion if, relying on the word of Kekule, he considers the latter to be the founder of the modern theory of constitution" [27].

In defending the priority of A.M. Butlerov, Markovnikov considered it necessary to publish a paper on the "History of the doctrine of chemical structure" also in a German journal [51]. In this paper, operating with facts, he demolished all attempts by Kekule to rob Butlerov of the credit for founding and developing the theory of chemical structure. This paper had a great effect on foreign chemists. It had a hostile reception among the supporters of Kekule who, in the absence of any factual data and scientific arguments in support of Kekule's priority, were unable to reply to it in print. However, on meeting Markovnikov they expressed their displeasure because of the publication of his paper. Apropos of this Markovnikov wrote as follows from Heidelberg to Butlerov:

"Concerning my paper about Kekule, there were no other unpleasantnesses apart from those about which I wrote to you. But even these were enough. It is difficult to prove that I said nearly the same in my dissertation because they are unable to read it. I told this to Erlenmeyer and he himself said that Baeyer believed on the contrary that you had written the paper" [52].

At the first meeting of Markovnikov with Baeyer an argument ensued about Markovnikov's paper on the "History of the doctrine of chemical structure". Markovnikov gave a full account of this argument:

"We argued the very first time. Baeyer asked whether I had really written the criticism of Kekule's book and when I answered in the affirmative I decided to go into battle. He reproached me with attacking Kekule as if he were a highwayman and toward the end I said: 'I wish you would also analyze Kekule's book, then you would see that nothing would remain of it' " [53].

Markovnikov informed Butlerov that Frankland in his papers ignored the theory of chemical structure and spoke only of the preparation by Butlerov of trimethylcarbinol [54].

Markovnikov wrote: "It is noteworthy that Frankland appears deliberately to be ignoring my work in all his papers. This is certainly because I am one of your pupils" [55].

And for many years afterwards Markovnikov continued to assert the indisputability of Butlerov's priority. In his inaugural lectures at the Novorossiysk University he declared:

"In speaking of the development of the theory of chemical structure, I pointed out that Kekule at first did not participate in its foundation. Soon, however, he published his well-known theory of aromatic compounds. In broad outline he did not put forward anything more than the application of the principles of chemical structure to the group of so-called aromatic substances, substances which are characterized by some fairly conspicuous features" [56].

The historical role of Butlerov in the founding and development of the theory of chemical structure was revealed, after Markovnikov, by D.I. Mendeleev [57] and by the most outstanding Russian chemists — S.V. Lebedev and others [58].

In his introductory lecture to the course on "Development and modern status of the doctrine of valence", delivered in Petersburg University on October 28, 1913, the celebrated Russian chemist S.V. Lebedev said:

"The fruit of the recognition of the quadrivalence of carbon, as I have already indicated, was the founding of the structural theory. The organic development of this theory is to the immortal credit of A.M. Butlerov" [59].

A vivid description of the scientific value of Butlerov's theory of chemical structure in the development of organic chemistry was given by A.E. Arbuzov in his address at the 5th Mendeleev Congress at Kazan in 1928. A high place was accorded to A.M. Butlerov, on the score of his creation of the theoretical bases of modern organic chemistry, in papers by A.I. Gorbov [60] and S.N. Danilov [61] published long before the historical surveys of recent years.

Russian chemists worthily continued the scientific-patriotic initiative of V.V. Markovnikov in asserting the priority of the great founder of the theory of chemical structure and, like Markovnikov, have creatively elaborated and enriched his notable scientific heritage.

In the thirties of the 19th century Dumas and Laurent detected the presence in organic compounds of "hydrogens" of diverse chemical natures — "metallic" and "metaleptic" hydrogens.

In the fifties of the 19th century N.N. Beketov proposed the principle of the "chemical value" of elements [62]. Beketov's principle showed that one and the same element has a different "chemical value" in different compounds due to the influence on it of other atoms or other groups of atoms present in these compounds.

Beketov wrote: "The carbon linked with hydrogen imparts to it quite a different chemical value (preferentially metaleptic) than the value it has in compounds with halogens in which it plays the part of a metal" [63].

Beketov's observation of the dependence of the chemical nature of an element on the chemical nature of the other elements present in a compound was the first step toward the understanding of the properties and reactions of inorganic and organic substances.

Logically following on Beketov's researches were the investigations of N.N. Sokolov on the question of the functional difference of atoms of hydrogen in chemical compounds. In studying the properties of lactic acid and of glycolic and glyceric acids (which he synthesized), Sokolov showed that hydroxy acids contain hydrogen atoms of diverse chemical natures — acidic and alcoholic. On the basis of his observations, Sokolov differentiated clearly between the concepts of basicity and valence of organic compounds. According to Sokolov, organic compounds contain all degrees of transition from metallic to metaleptic hydrogen [64]. In the light of Sokolov's ideas, the difference in character of hydrogen atoms is governed by their position in the molecule, the difference being intensified with increasing distance from one another in the carbon chain when the influence of the atoms falls.

"This difference, although completely specific, is not sharply defined between two atoms but is intensified with increasing distance of the members from one another; finally it becomes completely definite" [65].

N.N. Sokolov correlated the diverse chemical properties of hydrogen in organic compounds with the amount of caloric contained in them; this was the prototype of the contemporary doctrine of the store of energy of atoms. The views of N.N. Sokolov, generalized by much experimental material of organic chemistry, played an important role in the foundation of some premises for the doctrine of the mutual influence of atoms in a molecule, although they were limited by the framework of the unitary theory.

A.M. Butlerov highly valued the work of N.N. Beketov in theoretical chemistry. In proposing Beketov as corresponding member of the Academy of Sciences in 1877, Butlerov said:

"The principal studies and papers of Professor Beketov are distinguished by the outstanding feature that they concern the fundamental general problems of chemistry and consequently those whose solution is particularly important for the successful development of science. His very first paper, published in 1854 in the Bulletin of the Academy, related to "linked compounds and linking formulas" and thus concerned one such problem of organic chemistry" [66].

Even earlier Butlerov put a high valuation on the researches of N.N. Sokolov [67].

Beketov's ideas on the "chemical value" of elements and the views of Sokolov on the varying chemical nature of hydrogen in organic compounds were generalized, critically modified on the basis of the principles of chemical structure and raised to a higher level by A.M. Butlerov.

Butlerov's theory of chemical structure was the first to establish the existence of a definite order of bonds of atoms in a molecule, the direct and indirect bonds of atoms. It showed that the qualitative distinguishing feature of each molecule is determined not only by its composition but also by the order of the chemical bond of its atoms.

Butlerov declared: "The properties of a substance clearly indicate that each element exerts a specific influence upon the chemical content of the elements combined with it, and, conversely, is subject to the influence of the latter" [68].

Butlerov's theory was not restricted to the recognition of the chemical structure of molecules, the chemical interaction of atoms directly linked to one another. Butlerov's theory also indicated the occurrence in molecules of chemical interaction of atoms of another category – the reciprocal influence of atoms not directly linked together. Butlerov's structural formulas expressed the main, direct bonds and the principal chemical interactions of atoms in a molecule, characterizing the basic features of its chemical structure and chemical behavior. The problem posed by Butlerov about the indirect linkages in molecules governed the further development of the theory of chemical structure.

The main credit for the discovery of the laws of intramolecular mutual influence of atoms, for the founding and development of the doctrine of the mutual influence of atoms, belongs to V.V. Markovnikov. At the very start of his scientific activity, Markovnikov applied the principle of mutual influence of atoms to the study of the isomerism of allyl alcohol and its bromides, and also to the isomerism of oxygen-containing derivatives of propane [69].

The value of these investigations of Markovnikov for the establishment of the theory of chemical structure was noted by Butlerov in a specially written article [70].

In his magisteral dissertation (1865) Markovnikov quite clearly and definitely put forward the problem of the study of the reciprocal influence of atoms in chemical compounds as a chemical problem of the first importance.

He wrote: "The time has not yet arrived when we can accurately determine the degree of influence exerted by a given atomic grouping on all the chemical and physical properties of compounds".

"...Until we know all the internal and external conditions causing a substance to undergo metamorphosis, until we can determine what amount of chemical energy a given element contributes to the total amount of action, a knowledge of the true constitution will be impossible" [27].

With the objective of clarifying the various phenomena of reciprocal influence of atoms within a molecule, Markovnikov persistently and continuously studied numerous represenatives of the principal classes and groups of organic compounds and gradually accumulated experimental material obtained in a great variety of physical and chemical conditions.

Systematic investigations in this direction were undertaken in Markovnikov's laboratory under his guidance:

"Krivaksin will oxidize amylene chlorohydrin to obtain $ClH_2CCOC_3H_7$ or chlorovaleric acid, according to the mode of addition of the hypochlorous acid. Aleksandrysky will prepare isomeric dichloroacetone from dichlorohydrin. Sorokin is already studying the mode of arrangement of chlorine and iodine on their addition to unsymmetrical unsaturated hydrocarbons...In my opinion, only by such systematic work can we ever arrive, for some conditions at least, at an understanding of the influence of atoms and of their relative energy in reactions" [71].

Also in Germany the ideas of the mutual influence of atoms governed all his experimental investigations. From Leipzig Vladimir Vasilyevich wrote to Butlerov:

"I am sending my paper on acetonic acid to Annalen strictly because this is a good opportunity of enunciating some considerations about the mutual influence of elements in compounds on their chemical character. I again had to attack Kekule a little for the view he expressed about the order of substitution of hydrogen by chlorine in benzene. The paper has been lying with Kolbe for more than a week; he was going to correct it in respect of the language and always says"sometimes". By the way, I must tell you that I have now succeeded in convincing him of the impossibility of existence of two glycolic acids" [72].

In the forword to his doctoral dissertation on "Material for the problem of the mutual influence of atoms in chemical compounds" (1869) Markovnikov particularly stressed the indissoluble connection between the doctrine of mutual influence of atoms and the theory of chemical structure. He showed that the study of the interconnections and interdependences of the components of molecules broadens and deepens our knowledge of the chemical structure of organic compounds.

"The problem of the influence of atoms on the direction of chemical reactions of a compound is among the most exciting questions of modern chemistry and, as already noted, it is more and more holding the attention of chemists. It had naturally to arise as soon as the doctrine of chemical structure had been adopted by the majority, and it is a direct continuation and further development of this doctrine" [73].

V.V. Markovnikov defined mutual influence as the qualitative change of properties of one and the same atom in different chemical compounds: "The character of each component atom of a molecule is governed by the properties of the element with which it entered into combination, and vice versa" [73].

In studying the diverse changes of the chemical nature of atoms brought about under the influence of other atoms combined with them, Markovnikov discovered the chemical law: "The character of elements in compounds is governed not only by the elements directly linked to them but also by those which are associated with them in a chemical system through some other polyatomic element" [73].

The researches of Markovnikov established that the character and degree of reciprocal influence of not directly linked atoms depends on their position in the molecule, on the chemical nature of the surrounding atoms and on the distance separating them.

Markovnikov wrote: "In general the influence of any given element on another is weakened with increasing separation distance in the total chain of chemical action containing all the elements in the molecule" [73]. "...Hence (he concludes) in addition to qualitative and quantitative influences we have the influence of difference of arrangement..." [73].

On the basis of these general laws, Markovnikov conducted systematic investigations on the manifestation of the influence of each individual atom and each individual group of atoms on the chemical nature of the remaining atoms in a molecule. By this method Markovnikov established the theoretical rules for reactions of substitution, scission and addition which are known as the Markovnikov rules.

Subsequently Markovnikov revealed the connection between the reciprocal influence of atoms and the conditions of the external medium, which was a decisive step in the study of the directions and methods of study of chemical reaction.

In 1876 he formulated a general rule for reactions of addition to unsaturated molecules: "If an unsaturated molecule CmHnX combines with a saturated molecule YZ, at a relatively low temperature the negative element or group joins on to the least hydrogenated carbon or to the carbon already joined to the negative element (group), while at a higher temperature the addition takes place in the converse order" [74].

Markovnikov's work in the field of the reciprocal influence of atoms revealed to research workers entirely new methods in the study of molecules.

The theoretical rules of Markovnikov were guiding principles in the determination of the fine structure of organic substances, in the study of their reactions and most important transformations in nature and technology. They played an outstanding part in the development of the theory and practice of organic synthesis.

The notable investigations of Markovnikov's pupil, M.I. Konovalov, on the action of nitric acid on paraffinic hydrocarbons gave exhaustive proofs of the correctness of Markovnikov's rules for substitution in saturated hydrocarbons [75].

The doctrine of the reciprocal influence of atoms was born in the fight with metaphysical and mechanistic concepts in chemistry which regarded the molecule as a simple mechanical collection of atoms. Prominent representatives of Western European chemistry such as Kolbe, Erlenmeyer, Kekule, V. Meyer, Graebe, reduced the molecule to the sum of its component parts, denying the chemical interactions and interconnections of the components even as a whole in the molecule. In opposition to the principle of the reciprocal influence of atoms they supported the principle of additivity in chemistry. Applying this principle to problems of structure, they reduced the molecule to a simple mechanical chain of individual atoms, while they reduced the qualitative differences between atoms in molecules to purely quantitative differences.

Graebe (a well-known pupil of A. Baeyer) thus asked Markovnikov:

"Why does the chlorine in acetyl chloride differ so markedly from chlorine in ethyl chloride ?"

Markovnikov wrote: "I cannot fail to remember this, nor the numerous and prolonged debates which I had with Kolbe... Already in the first year of my stay in Germany I was convinced that the Kazan laboratory was theoretically a long way ahead of all the German laboratories" [76].

As V.V. Markovnikov indicates, his concepts confirmed the qualitative differences between identical atoms in different molecules; "the laws derived therefrom, confirmed by many important reactions, were then completely novel or even conflicted with extremely authoritative concepts (of Kekule)" [77].

The metaphysical conception of the world of West European chemists – supporters of the idealistic philosophy of Kant – prevented them from understanding the doctrine of the reciprocal influence of atoms which raised to a new qualitative level our knowledge of the structure of organic and inorganic substances and enabled a deeper penetration into the interior of their molecules.

The scientist-materialist V.V. Markovnikov regarded the molecule as a self-balanced dynamic system of interacting atoms. He states that "the existence of molecules with properties known at a given instant is the result of the mutual influence of its atoms. In specified conditions these influences must be identically balanced, otherwise we should not be able to conceive why, in identical conditions, a molecule always has the same properties. The study of these conditions is one of the main problems of chemistry" [78].

The intramolecular reciprocal influence of atoms and the stability of molecules are indissolubly linked, in Markovnikov's opinion, with the external conditions (temperature).

From his studies of molecular dynamics and the interaction of the component parts of molecules, Markovnikov established that chemism is motion. He regarded the chemical form of motion as a special type of motion, a qualitatively different form of motion: "Just as heat and light are manifestations of a known form of motion of material particles, so is chemism also motion. The difference may perhaps reside merely in...the type of motion" [79].

Developing a materialistic trend in chemistry, V.V. Markovnikov is compelled to reject the notions of absolute peace in nature, of the immobility and immutability of chemical compounds.

As early as 1872 he posed the question of the physical – spatial – arrangement of atoms in molecules. In his inaugural lecture at Novorossiysk University Markovnikov says: "It is difficult, however, to conceive that there are not direct and specific relations between the chemical interaction and the physical position of the atoms in a molecule. There are certainly some facts which very strongly support the idea of the existence of such relationships" [79].

The doctrine of the mutual influence of atoms enabled Markovnikov also to be the first to correctly illuminate the problem of free radicals. In his report of 1902 he pointed out: "All the chemical properties of $(C_6H_5)_3C-C(C_6H_5)_3$ are easily accounted for on the assumption that the fourth unit of affinity of the C requires, for satisfaction of its chemical avidity, another affinity than that which may be available to it from the C linked with the three C_6H_5's. Hence the bond between the carbons in R_3C-CR_3 will be easily ruptured, allowing formation of derivatives of the $(C_6H_5)_3C$ radical which are capable of existing. We may here expect different syntheses provided the fourth C unit is satisfied by the appropriate affinity" [80].

In those days foreign chemists, headed by Gomberg, considered hexaphenylethane to be an extremely stable compound, and the views of Markovnikov on the dissociation of hexaphenylethane into two free radicals were in sharp conflict with the generally accepted point of view. Markovnikov's ideas about the structure of hexaphenylethane were experimentally confirmed and developed by his pupil A.E. Chichibabin [81].

In 1904 Chibibabin began his investigations of the structure of triphenylmethyl.

He writes: "The idea of quadrivalence or at least of uneven valence of carbon was firmly fixed in the minds of the overwhelming majority of organic chemists in the whole of the preceding dazzling period of development of organic chemistry. I therefore embarked on the investigation, being deeply certain of the inaccuracy of

Gomberg's explanation of the structure of the hydrocarbon. At the same time I doubted somewhat whether without any assistance I could actually demonstrate beyond all question the error of Gomberg and find the true explanation of the phenomenon discovered by Gomberg.

"The first of my tasks was to show the validity of that formula for triphenylmethyl with quadrivalent carbon which seemed to me to be particularly probable, i. e. the formula of hexaphenylethane. This task was carried out with full success.

"The second problem was to find phenomena, similar to the striking phenomena discovered by Gomberg for triphenylmethyl, among other substances possessing an undisputed structure. This problem, too, was solved in my opinion by the investigation and discovery of some striking properties of pentaphenylethane" [82].

The outstanding value of the investigation of A. E. Chichibabin in the discovery of free radicals and in the detection of trivalent carbon was mentioned by S. V. Lebedev at the inaugural lecture at Petersburg University (1913):

"At this moment, thanks to the efforts of Gomberg, Chichibabin, Schlenk and others, the problem has gone beyond the bounds of any doubts — trivalent carbon exists" [83].

The development of electronic concepts in organic chemistry led to widening and deepening of the laws of intramolecular reciprocal influence of atoms discovered by Markovnikov, to the discovery of the nature of the chemical bonds in various classes of organic compounds.

The ideas and researches of V. V. Markovnikov live on and go on developing in our day, for they are a powerful aid and driving force for the solution of fundamental chemical problems.

The name of Vladimir Vasilyevich Markovnikov can with full justification be grouped in the history of science side by side with the names of A. M. Butlerov and D. I. Mendeleev.

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MECHANISM OF HYDROGEN EXCHANGE AND OF SOME PROTOLYTIC REACTIONS IN SOLUTIONS

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In a previous paper [1] general considerations were put forward about the modes of isotopic exchange of hydrogen in solutions. They can now be corroborated and developed in more detail as a result of investigations which were subsequently undertaken. The problem of the mechanism of hydrogen exchange is of general interest since it is associated with the important problem of the mechanism of many hydrogen transfer reactions and in particular with protolytic reactions in solutions.

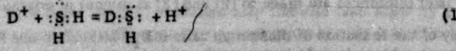
I. Rapid and Slow Exchange

Depending upon their ability to undergo hydrogen exchange in solutions, numerous investigated compounds [2, 3] form two sharply differentiated groups. In the first of these the exchange proceeds substantially instantaneously at any given temperature without need for a catalyst. This is true of the N–H, O–H, S–H, Cl–H bonds and many others, although not of all compounds with acid-base donors of deuterium, for example, with D_2O, C_2H_5OD. We propose to call this the rapid type of exchange. In the second group of compounds, exchange either does not take place at all or it only proceeds more or less slowly. The possibility of its occurrence and its velocity are determined by the structure of the molecules and by the nature of the substituents present, by the reaction of the medium and by the properties of the deuterium donor. Exchange of this type (which we call slow) exhibits a strong dependence upon the temperature and upon the presence of catalysts for protolytic reactions. The slow type of exchange is characteristic of the C–H bonds in organic compounds. From the table we see that the type of exchange is not governed either by the properties of the individual bonds in which the exchange proceeds or by the nature of the atom with which the exchanging atom of hydrogen is directly linked. In particular, contrary to the prevalent conception, it is not characterized by the energy, by the polarization, or by the "ionic quota" of the bond.

TABLE

Bond	Bond energy	Length of bond	Dipole moment	Atomic refraction	Constant of bond strength $f \cdot 10^{-5}$	Difference of electro-negative activity
N–H	83.7	1.01	1.31	3.42	7.1	0.98
C–H	87.3	1.09	0.4	3.52	5.1	0.52
S–H	87.5	1.35	1.03	8.79	4.0	0.41
Cl–H	102.7	1.28	0.68	7.07	5.1	0.98
H–H	103.4	0.74	0	2.20	5.1	0
O–H	110.2	0.97	1.51	2.63	7.5	1.33

Rapid or slow exchange in the bond of X–H is determined by the presence or absence of free (unsaturated) electronic pairs round the atom X. If these are present, then a deuteron (or proton) may add on to one of them with simultaneous detachment of a proton from the electron pair linked with the other. This process, whose mechanism is considered in detail below, can be represented by the following scheme for, for example, exchange between H_2S and D_2O:



$$D^+ + :\underset{H}{\underset{..}{\ddot{S}}}:H = D:\underset{H}{\underset{..}{\ddot{S}}}: + H^+ \qquad (1)$$

It takes place in a single elementary act and evidently does not require an appreciable activation energy. Hence the exchange takes place very quickly even at low temperature. In the absence of a free electron pair, as for example in the C − H bonds of organic compounds, the deuteron can only add on at the same electron pair to which the proton is bound, after elimination of the latter. This process demands a considerable activation energy and exchange proceeds either slowly or not at all, depending upon the factors determining the strength of the C− H bond and its ability to release a proton. Various mechanisms possible for this process are considered below. With the objective of confirming these ideas, several fresh examples of hydrogen exchange were studied in our laboratory. In the Si−H bonds of organosilicon compounds, there are no free electron pairs round the silicon atom and no hydrogen Exchange is manifested in them. In a paper by Khaskin and the author [4] the absence was shown of exchange in triethyl-, triphenyl- and triethoxysilanes $(C_2H_5)_3SiH$, $(C_6H_5)_3SiH$ and $(C_2H_5O)_3SiH$ with D_2O, C_2H_5OD and $(CH_3)_2ND$ even on prolonged heating above 100 deg. This result could not have been predicted on the basis of analogy with exchange in the corresponding tertiary carbon compounds since the Si−H and C−H bonds differ very markedly not only in strength but also in the sign of polarization [5]. In ammonia, various amines and amides [6], possessing a free electron pair round the nitrogen atom, indications of slow exchange were not detected in a single instance, whereas in the ammonium ion the exchange has a measurable kinetics and takes place in the process of hydrolysis with participation of ammonia. This is confirmed by the dependence, found by Sulima and the author [7], of the exchange velocity in ammonium salts on the presence of concentrated strong acids which suppress hydrolysis. This mechanism occurs in slow exchange in the $Co:NH_3$, $Pt:NH_3$ and $Pd:NH_3$ bond of the series of hexammino- and tetrammino- salts whose kinetics depend largely on the pH of the solution [3] *. Hypophosphorous and phosphorous acids have the well-authenticated structure of $O{=}PH_2(OH)$ and $O{=}PH(OH)_2$ corresponding to the absence of a free electron pair round the phosphorus atom. In harmony with this, Sulima and the author [9] found that exchange with D_2O does not occur in the P−H bond of phosphorous acid and its anion and only proceeds very slowly in hypophosphites at 100 deg. In hypophosphorous acid, however, it proceeds in the P−H bond even at 25° with a half-period of 16 minutes. It is impossible on the basis of only the reciprocal influence of atoms to explain these large differences in the exchange susceptibility in such similarly constituted substances. Exchange in hyposphosphorous acid is associated with its tautomeric transformation into the $HP(OH)_2$ form, as is confirmed by a comparison of its exchange and oxidation kinetics. **

According to some literature date [3] gaseous H_2 does not exchange hydrogen for the deuterium of heavy water in the absence of catalysts promoting cleavage of the H:H molecule. Exchange also does not occur in the B−H bonds of borohydrides not possessing a free electron pair round the boron atom; nor is there exchange between BH_4^- and D_2O [13] and between $B_2H_6 \cdot ND_3$ and liquid ND_3 [3].

The now known cases of slow hydrogen exchange are limited to the examples considered and to numerous examples of exchange in the C−H bonds of diverse organic compounds. They are all characterized by the absence of free electron pairs round the atom with which the exchanging hydrogen atom is linked. On the other hand, not a single case is known*** where exchange would proceed very quickly if such pairs were present. We can therefore claim that the considerations here discussed are sufficiently well founded.

II Mechanism of Rapid Exchange

Rapid exchange of hydrogen between a substance XH (see * on next page) and heavy water (or other deuterium donor with acid-base functions) is usually explained by electrolytic dissociation:

$$XH + D_2O = X^- + HD_2O^+ = XD + HDO, \qquad (2)$$

if XH is an acid, or

$$XH + D_2O = DXH^+ + OD^- = XD + HDO, \qquad (3)$$

if XH is a base relative to water (or the dissolved catalyst). However, an unmeasurably high velocity of exchange is observed even with extremely weak acids and bases and it is not appreciably slowed down by addition of a large excess of strong acids or bases when the equilibrium concentrations of the products of dissociation of XH fall to 10^{-10} and lower. Such low concentrations of ions cannot lead to rapid exchange.

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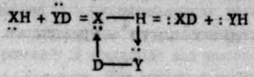
* Here and later references are made to [2] and [3] as sources of original literature.

** In a study of the reduction of diazonium salts in D_2O Miklukhin and Rekasheva [11] also found slow exchange in the P−H bonds of hypophosphorous acid. In a recent investigation Jenkins and Yost [10] obtained results in agreement with ours for exchange of H_3PO_2 with T_2O. In their paper exchange was also explained by tautomerism, although only on the basis of the above-mentioned comparison of the exchange and oxidation kinetics.

*** Apart from indication [12] of slow exchange between gaseous PH_3 and liquid D_2O, the kinetics of which is possibly determined by the diffusion of the poorly soluble phosphine in the bulk of the solution.

It is necessary to assume that rapid exchange proceeds independently of the electrolytic dissociation of (2) or (3) (which is not the cause of the rapid type of exchange) and of the simultaneously proceeding parallel reaction (also capable of leading to exchange), and that therefore the velocity of rapid exchange is not directly associated with the strength of the acids and bases taking part in the exchange. According to the considerations here advanced, rapid exchange between substance XH and a deuterium donor YD is effected in a single elementary act through the intermediate state (a) by simultaneous transfer of a proton to the free electron pair of atom Y and of a deuteron to the same pair of atom X:



$$\ddot{X}H + \ddot{Y}D = \underset{\underset{D\text{———}\ddot{Y}}{\uparrow\qquad\downarrow}}{\ddot{X}\text{———}H} = :XD + :YH \qquad (4)$$

(a)

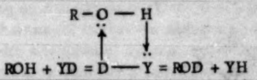
This symmetrical process does not require a high activation energy apart from that expended on a favorable orientation of the exchanging molecules and on equalizing the interatomic distances of X−H and Y→D. The activation energy of anomalous electronegativity, according to Grotthus, possessing a similar mechanism, is only 2-3 kcal/mole as calculated from its temperature coefficient. On the other hand, the symmetrical structure of the intermediate state and the encirclement by molecules of solvent exclude abnormally low values of the exponent. Reactions with these characteristics proceed unmeasurably fast even at low temperature. Exchange according to scheme (1), which differs from (4) by the participation of three molecules in one elementary act, may proceed in a strongly acidic medium with a large excess of hydroxyl ions.

Electrolytic dissociation (2) may be represented, taking account of solvation of ions, by the following exemplary scheme:

$$YD + XH + YD = YD\ldots\overset{-}{X}\ldots\overset{+}{H}\ldots YD = YDX^{-} + HYD^{+}. \qquad (5)$$

Unlike (4) this process requires considerable energy for scission of the X−H bond, which is compensated to a greater or lesser degree by the energy of solvation of the ions. Its activation energy depends both on the properties of the scissionable bond and on the energy of interaction of the solvent of YD with the solvatable ions. These account for the diverse values of the strength of acids and bases in dependence upon their structure and the solvent; they also account for the diverse rates of dissociation which proceeds more slowly, for instance, in C−H bonds. The very low acidity of hydrocarbons is apparently due to the absence of free electron pairs, so that the energy of cleavage of a proton from the C−H bond is not compensated by the simultaneous covalent addition of a molecule of the solvent to the formed carbanion according to scheme (5).

In hydroxyl compounds rapid exchange is likewise not associated with the formation of free hydroxyl ion, while in presence of free electron pairs it proceeds by the same mechanism (4):



$$\begin{array}{c} R-\ddot{O}\text{ — }H \\ \uparrow\qquad\downarrow \\ ROH + YD = D\text{——}\ddot{Y} = ROD + YH \end{array} \qquad (6)$$

For example, in ethyl alcohol an exchange equilibrium is rapidly established with D_2O [14].

Attention has already been drawn by Miklukhin [16] to the role in hydrogen exchange of intermediate complexes formed by hydrogen bonds.

Exchange of water with liquid ND_3, DBr, D_2S, etc. does not introduce any fundamental changes into these schemes. The acidic or basic properties of these solvents, of decisive importance for the slow type of exchange, should not play an important role in the rapid type of exchange.

III Mechanism of Slow Exchange

In the absence of free electron pairs round atom X, exchange may likewise take place by a mechanism formally identical with (4), but with the important difference that a deuteron may only join on covalently to that electron pair which previously bound the proton and only after the removal of the latter has freed the pair.

• Here and later, for the sake of simplicity, the symbols XH and YH used to denote both the exchanging bonds and the exchanging molecules themselves.

This process has a considerably higher activation energy than is the case in the rapid type of exchange. In the intermediate quaternary complex formed by hydrogen bonds, such a proton transition does not occur at all or is greatly slowed down in dependence on the height of its potential barrier. The latter is determined by the structure and arrangement of the electronic densities in the exchanging molecules; it is also influenced by the properties of the medium, whereas these factors have little importance for rapid exchange.

The ratio of the velocities of electrolytic dissociation of (2) or (3) and of the type (4) process determines the mechanism of slow exchange. If electrolytic dissociation is the faster process, then exchange takes place through the stage of formation of free ions according to the scheme:

$$XH + YD = X^- + HYD^+ = XD + YH \qquad (7)$$

in an alkaline medium, or

$$XH + YD = DXH^+ + Y^- = XD + YH \qquad (8)$$

in an acid medium, and other intermediate stages are possibly involved. This is usually referred to as the ionization mechanism. But if a type (4) process proceeds more quickly than electrolytic dissociation, then exchange is accomplished in a single act via the intermediate complex formed with hydrogen bonds and not with covalent bonds:

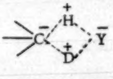
$$XH + YD = \begin{array}{ccc} X & \cdots & H \\ \vdots & & \vdots \\ D & \cdots & Y \end{array} = XD + YH. \qquad (9)$$

This is usually known as the association mechanism. Both mechanisms are very common in the C—H bonds of organic compounds, and the rest of this paper will be devoted to their consideration.

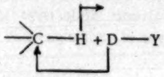
IV. The Association Mechanism

Due to the great electrophilicity of the proton, the association mechanism of hydrogen exchange resolves itself into a mechanism of electrophilic substitution. Systematic study of the exchange with deuteroacids in aromatic compounds has shown that it is facilitated by the same factors which facilitate electrophilic substitution (sulfonation, nitration, halogenation, etc.), namely, high acidity of the deuterium donor and of the substituent which increases the electron density at the carbon atom in the C—H bond in which the exchange is proceeding. For example, Shatenshtein [17] showed that exchange of hydrocarbons with liquid deuterium bromide is accelerated by introducing electropositive substituents, $-CH_3$ and $-OCH_3$, and is slowed down by introducing electronegative substituents, $-CN$ and $-NO_2$.

In typical cases the electrophilic substitution of hydrogen proceeds apparently via the intermediate quaternary complex



but we must also reckon with the possibility of other mechanisms of electrophilic substitution entering into consideration in organic chemistry, for example:



with participation of a third molecule.

Comparison of the rate of exchange of benzene with pure and dilute D_2SO_4 [15] and other date confirm that free hydroxyl ions are not involved in the association mechanism. This markedly differentiates it from the ionization mechanism (8) in an acidic medium. Other differences between both mechanisms will be indicated below.

V. The Ionization Mechanism

The ionization mechanism must be considered typical of slow exchange with basic donors. It is favored by factors which facilitate the first ionization step - basicity of the medium or the presence of basic catalysts and substituents reducing the electronic density at the carbon atom in the exchanging C−H bond. The influence of substituents, as we know, is manifested in a complex manner and cannot by any means always be precisely predicted. We can cite a number of examples, however, in which it is simply correlated with the exchange susceptibility [2, 3]. Methane, ethane and benzene do not exchange hydrogen with water, but in nitromethane, nitroethane, nitroethane and 1,3,5-trinitrobenzene, exchange takes place and is catalyzed by alkalies. The former are capable of rearranging into aci-forms with detachment of a proton from the C−H bond. In presence of alkali, exchange also proceeds in acetamide and acetonitrile. In these examples electrons are attracted by the negative NO_2 CN and CO groups. The enhanced ability of the C−H bond to undergo ionization round the ternary C≡C bond is manifested in the facility of exchange of acetylene with water in presence of alkali. In exchange by the ionization mechanism an extremely important part is played by $\sigma - \pi$ conjugation, whose importance for various organic chemical reaction has been demonstrated by Nesmeyanov [19]. The dependence of exchange of α-hydrogen on the conjugation in the H−C−C=O chain was confirmed by Nesmeyanov, Kursanov and co-workers [20] in cyclic ketones, acetylacetonates and dibenzoylmethane, and later by Shatenshtein [23] in hydrocarbons. Exchange in the methylene group of acetylacetone and ethyl acetate proceeds considerably faster than in acetone due to the participation of two C=O groups linked to the α-carbon in the conjugation. For the same reason exchange proceeds relatively easily in the methylene group of malonic esters and ethyl cyanoacetate, which may be correlated with their known facility of condensation with carbonyl compounds. In acetates the conjugation in two chains − the H−C−C=O chain and the M−O−C=O chain − comes simultaneously into play and, as Mikhulin [22] showed, exchange in their methyl group proceeds with greater facility the lower the polarity of the M−O bond. Conjugation of the C−H bond with the nucleus in the methyl group of toluene is insufficient for exchange in the latter with water, but in our laboratory we found [31] that exchange proceeds in nitrotoluenes and is catalyzed by alkalies, as was to be expected.

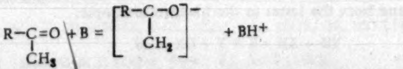
Up to recently the study of hydrogen exchange in the liquid phase had been almost entirely restricted to aqueous solutions where the acidic properties of the C−H bond are manifested only to a very minor extent and their differences are largely equalized. Recent papers by Shatenshtein and co-workers [23] deal with the slow hydrogen exchange of many hydrocarbons in liquid ND_3 which is a much stronger base than water. In it, especially in presence of the even stronger base, potassium amide, exchange takes place with greater facility than in water, and its velocity quantitatively characterizes the acidity of the hydrocarbons [24]. The difference between mechanisms (7) and (9) is particularly clearly manifested by the inhibiting effect of substituents on the exchange of hydrocarbons with ND_3 and DBr. All these, as well as a series of other data, confirm the modes of slow hydrogen exchange in solution here discussed.

VI. Steps of the Ionization Mechanism

The ionization mechanism of exchange (8) in an acid medium is typical of carbonyl and certain other compounds capable of adding on a proton to the C=O, C=N, etc. bonds. It differs fundamentally from the associative electrophilic mechanism (9) in that the addition of a proton (or deuteron) and exchange take place at different carbon atoms with migration of the reaction center [19] and in separate steps.* In the first, usually rapid, step a proton is transferred from the acidic solvent or catalyst to the dissolved molecule. In the resultant onium cation the neighboring C−H bond is weakened and this leads to exchange or to other protolytic reactions involving one or more slower steps. This general scheme is confirmed by a series of kinetic studies [3].

There are insufficient well-founded experimental data about the individual intermediate steps of exchange according to the ionization mechanism (7) and in particular (8). Various schemes have been advanced for these and other protolytic reactions; we shall consider only the most typical of these [3, 16, 18, 26]. Their comparison may give a criterion of their reliability.

There is such a great similarity between hydrogen exchange, enolization, racemization and halogenation of ketones in presence of bases that an identical mechanism must be assumed for the first slow step: transition of proton from the C−H bond to the base B:



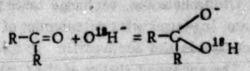
$$R-\underset{\substack{|\\ CH_3}}{C}=O + B = \left[R-\underset{\substack{|\\ CH_2}}{C}-O \right]^- + BH^+ \qquad (10)$$

---

* The difference between mechanisms (8) and (9) roughly corresponds to the difference between a "bimolecular" (S_E2) mechanism and a "monomolecular (S_E1) mechanism (to use the terminology of the English school [18]). This terminology cannot be considered a happy one since a solvent or catalyst usually participates in the reaction and this renders very indeterminate the difference in the molecularity and kinetic order of the slow step.

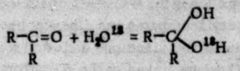
The reverse reaction (10) with BD^+ leads to exchange, while addition of a proton to the oxygen leads to enolization. The duality of the reaction of the intermediate ion is explained, according to Nesmeyanov [19], by transfer of a reaction center on the conjugated chain from the α-carbon to the carbonyl oxygen under the influence of the reagent, and does not require to be explained by any fundamentally inaccurate or sterile resonance or mesomerism concepts.

This mechanism is confirmed by many experimental facts, but it is unsuitable for oxygen exchange of ketones with H_2O^{18} in presence of alkalies because it evidently does not lead to such an exchange. For the latter it is suggested that the slow step is the addition of hydroxyl to the carbonyl carbon:



(11)

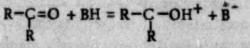
followed by migration of a proton from one oxygen atom to the other and later by addition of a proton (from the alkaline solvent) with formation of a symmetrical orthostructure $R_2C(OH)_2$. In order to get round these difficulties, some authors prefer a mechanism of primary addition of water at the double carbonyl bond:



(12)

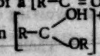
Such primary steps as (11) or (12) with diverse variants of the succeeding steps are assumed for reactions of hydrolysis of carboxylic esters, oxygen exchange in aldehydes, carboxylic acids and their esters, etc. in presence of bases or in a neutral nedium. In D_2O^{18} however, acetone exchanges both hydrogen and oxygen with commensurate velocities [25]. On the basis of the mechanisms considered, it is necessary to assume that we have simultaneously, and with similar velocities, the reaction (10) of detachment of a proton and reaction (11) or (12) of addition of hydroxyl ion or water. The unsatisfactory character of such a hypothesis indicates the dubiousness of these mechanisms.

Even greater difficulties stand in the way of a detailed knowledge of mechanism (8) of isotopic exchange and other protolytic reactions of carbonyl compounds in presence of acidic catalysts. For the above-mentioned reactions of ketones, the first (rapid) step is considered to be the transfer of a proton from the acid BH to carbonyl oxygen:



$$\underset{\displaystyle R}{\underset{|}{R-C}}=O + BH = \underset{\displaystyle R}{\underset{|}{R-C}}-OH^+ + B^- \qquad (13)$$

Addition of a proton to carbonyl weakens the neighboring C−H bond and the proton can transfer from it to water with formation of an enol. Transfer of a proton from the C−H bond to the base remains the slow step if we ignore the cases of a very weak acid BH and molecules with a very strongly polarized C−H bond. This mechanism accounts for enolization but not for exchange, for which it is necessary to assume subsequent steps with participation of the enol. Consequently, in an alkaline medium, hydrogen exchange is regarded as a reaction proceeding in parallel with enolization and independently of it; in acid medium it is considered to proceed via the enolization step. Such a dualism is likewise doubtful.

For the hydrolysis of carboxylic esters in presence of acids after a step analogous to (13), further steps with participation of water are necessary. Various suggestions have been made apropos of the latter and they can be reduced to three fundamental variants [26]: 1) cleavage of alcohol with formation of a $[R-C=O]^+$ ion, ion, followed by addition of water to it; 2) exchange of a proton for an alcohol radical between  and water; 3) addition of water to the same ion with formation of the orthoester of the monocarboxylic acid, which then splits off alcohol. Esterification reactions proceed trhough the same steps in the reverse order. Similar schemes explain the oxygen exchange in ketones and carboxylic acids; in this connection, for consistency with kinetic data and the presence of general acid catalysis, we must assume the slow step of transfer of a proton from acid to carbonyl or from the latter to the base conjugated with the acid BH [25]. Both are equally unlikely.

The unsatisfactory nature of all these schemes induced some authors [18, 27] to revert to the old trimolecular mechanism of Lowry, according to whom a proton (or deuteron) is transferred in one elementary act from acid to substrate and from the latter to the base, for example:

$$YD + XH + B = Y + DX + HB. \qquad (14)$$

This mechanism in turn was rejected because the kinetic equations did not contain a term corresponding to it involving the product of three concentrations, but such a conclusion cannot be considered convincing. In particular the trimolecular mechanism of exchange of hydrogen between alkenes and ND_3 was confirmed by

Shatenshtein [23] who found that exchange is accompanied by isomerization with rearrangement of the double bond.

If the deuterium donor YD and the acceptor B are different reaction centers in the same molecule, then mechanism (14) is similar to mechanism (9) for slow exchange.

VII. Exchange in radicals

Reactions in solutions with participation of free radicals are very common, and we may suggest that a radical mechanism is also encountered in reactions of hydrogen exchange of dissolved substances. This problem is intimately associated with the study of the hydrogen bond in free radicals about which very little is yet known.

Kursanov and co-workers [28] found that saturated aliphatic hydrocarbons exchange all the hydrogen atoms with concentrated D_2SO_4 if they contain tertiary carbon, and that exchange does not take place if the latter is absent. They explain this by a chain process with participation of $R_3C^{\cdot}$ radicals or of R_3C^+ ions, resulting in rearrangement of the chain and rapid exchange of hydrogen with the acid during the period of their brief existence. Such an exchange demands mechanism other than those considered above. If exchange proceeds in the carbonium ion, then the weakening of the C—H bond by the positive charge of the ion is probably insufficient to account for the rapid exchange. But if it proceeds in the radical, then we can explain the mechanism on the basis of the observation, by Fomenko and Sadovinkova [29], of absence of exchange in triphenylmethyl with D_2O or $(CD_3)_2CO$ even after prolonged heating at 100°. Unambiguous data were likewise not obtained for exchange of radicals with D_2O in a study of Kolbe's electrochemical synthesis with the help of deuterium [16].

Until new experimental data are obtained, another question which remains open is that of the role of transfer of radicals or atoms of differing isotopic composition in hydrogen exchange in solutions. Also requiring study is the possibility of participation of hydride anions in the exchange.

SUMMARY

1. A classification of reactions of isotopic exchange in solutions is advanced which is confirmed by experimental data. Such reactions are of the slow or fast type depending upon the presence or absence of free electron pairs round the atom with which the exchanging hydrogen atom is linked.

2. Exchange of the rapid type proceeds independently of the electrolytic dissociation — a process taking place in parallel.

3. The fundamental mechanisms of the slow type of exchange are discussed.

4. The unsatisfactory features of previously advanced mechanisms of protolytic reactions of carbonyl compounds are demonstrated.

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THIOSULFATE COMPLEXES OF MERCURY

V. F. Toropova

Thiosulfate complexes of mercury were described long ago in the literature. The following compounds were obtained in solidform:

$$5K_2S_2O_3 \cdot 3HgS_2O_3;\ 3K_2S_2O_3 \cdot HgS_2O_3 \cdot 3H_2O;\ 5K_2S_2O_3 \cdot HgS_2O_3 \cdot H_2O\ [1].$$

The process of formation of complexes of divalent mercury with the thiosulfate radical in aqueous solutions has been utilized for potentiometric titration of the thiosulfate ion with mercuric chloride solution [2]. The maximum potential change corresponded to formation of the complex ion $[Hg(S_2O_3)_2]^{2-}$. The existence of these complex anions was confirmed by Kolthoff and Miller by investigation of the polarographic waves obtained during anodic polarization of the dropping mercury electrode in sodium thiosulfate solutions [3]. The anodic wave is appreciably shifted in the direction of the negative potentials, which indicates high stability of the complex formed. The stability of this complex, however, was not studied.

The thiosulfate residue is a strong coordinated substituent, belonging according to Yatsimirsky's classification to the covalent addends [4].

The thiosulfate complexes of many metals are distinguished by high stability. The values of the instability constants are only known for a few complexes, including the complexes of some divalent metals (Cd^{2+}, Zn^{2+}, Pb^{2+}). Cadmium ions form the complexes $[Cd(S_2O_3)_2]^{2-}$ ($K = 5.3 \cdot 10^{-5}$); $[Cd(S_2O_3)_3]^{4-}$ ($K = 1.6 \cdot 10^{-6}$).

The instability constant of the thiosulfate complex of zinc is equal to $5 \cdot 10^{-3}$ [5]. Thiosulfate complexes of lead are characterized by the following values of constants:

$$K_{[Pb(S_2O_3)_2]^{2-}} = 7.4 \cdot 10^{-6}; \quad K_{[Pb(S_2O_3)_3]^{4-}} = 4.5 \cdot 10^{-7}\ [6].$$

Grinberg and Yatsimirsky [7] observed that for the covalent type of bond the stability of the complexes formed by ions of subgroups of the periodic system of D.I. Mendeleev increases with the atomic number of the element. Consequently, thiosulfate complexes of mercury must be more stable than the corresponding complexes of cadmium and zinc.

This paper deals with an investigation of the composition and stability of complexes formed with ions of divalent mercury and thiosulfate ions.

EXPERIMENTAL*

Thiosulfate complexes of mercury were studied by the potentiometric method using a Hartmann and Braun potentiometer. A type GZS–47 mirror galvanometer served as the zero instrument.

The indicator electrode was metallic mercury which had been twice distilled in vacuum. The comparison electrode was a saturated calomel electrode with a potential of 0.244 V relative to the normal hydrogen electrode. The siphons for the electrolytic contacts were filled with 3% agar-agar solution in a saturated potassium nitrate solution. The intermediate electrolyte was a saturated potassium nitrate solution. The starting solution of mercury nitrate was prepared by dissolving 2 g vacuum-distilled mercury in 5 ml conc. nitric acid (d 1.2) and was diluted with water to 1 liter. The concentration of divalent mercury ions in the test solutions was 10^{-3} g-ion/l and $2 \cdot 10^{-3}$ g-ion/l.. Sodium thiosulfate solutions were prepared from the chemically pure salt. The titers were determined by the iodometric method (with potassium bichromate). The test solutions were made up by the following procedure: To a measured volume of $Hg(NO_3)_2$ solution (2.5 or 5 ml) was added the equivalent amount of alkali for precipitation of mercuric oxide, which was then dissolved in a definite amount of sodium thiosulfate solution. The resultant solution was made up to the mark in a 25 ml measuring flask.

Measurements of potentials of the mercury electrode in the investigated solutions were carried out in a water thermostat at a temperature of 25 ± 0.05°.

Results of potential measurements are set forth in Tables 1 and 2.

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* K. M. Skoryskaya participated in the experimental work.

TABLE 1

Potentials of the Mercury Electrode in Solutions of Complex Mercury Thiosulfates at Low Concentrations of Sodium Thiosulfate.
Initial concentration of $Hg^{2+} = 10^{-3}$ g-ions/liter

Molar concentration of $Na_2S_2O_3$	Activity coefficient of $Na_2S_2O_3$ [13]	$-\log a_{S_2O_3^{2-}}$	Potential of mercury electrode $-E_{Hg}$ (in V)
$3.94 \cdot 10^{-3}$	0.77	2.516	0.1749
$5.91 \cdot 10^{-3}$	0.73	2.364	0.1869
$6.69 \cdot 10^{-3}$	0.715	2.320	0.927
$7.88 \cdot 10^{-3}$	0.69	2.262	0.2005
$9.85 \cdot 10^{-3}$	0.67	2.182	0.2090
$1.97 \cdot 10^{-2}$	0.565	1.953	0.2367
$3.94 \cdot 10^{-2}$	0.49	1.714	0.2633

TABLE 2

Potentials of the Mercury Electrode in Solutions of Complex Mercury Thiosulfates with Excess of Sodium Thiosulfate.
$C_{Hg^{2+}} = 2 \cdot 10^{-3}$ g-ions/liter

Molar concentration of $Na_2S_2O_3$	γ [13]	$-\log a_{S_2O_3^{2-}}$	$-E_{Hg}$ (in V)
$3.91 \cdot 10^{-2}$	0.49	1.717	0.2537
$7.82 \cdot 10^{-2}$	0.47	1.435	0.2817
$1.17 \cdot 10^{-1}$	0.45	1.278	0.2980
$1.56 \cdot 10^{-1}$	0.416	1.186	0.3105
$1.95 \cdot 10^{-1}$	0.386	1.122	0.3108
$3.13 \cdot 10^{-1}$	0.338	0.979	0.3334
$3.91 \cdot 10^{-1}$	0.316	0.908	0.3420
$6.26 \cdot 10^{-1}$	0.272	0.769	0.3577

Determination of the Composition and Instability of Complex Ions

The composition of complexes formed in solutions may be determined from the curve of electrode potential against the logarithm of the activity of the complex-forming salt [8].

The curves plotted from the data of Tables 1 and 2 are convex to the abscissas. This indicates the stepwise character of complex formation. At higher concentrations of sodium thiosulfate (above 0.2 M) the plot of change of potential of the mercury electrode against the logarithm of the activity of $S_2O_3^{2-}$ becomes nearly a straight line. The experimental points fit on a straight line with an angular coefficient of 0.119. We thus obtain the following value for the number of coordinated groups n:

$$\bar{n} = \frac{\tan \alpha}{0.0295} = 4.03.$$

Evidently in these conditions a complex anion of the composition $[Hg(S_2O_3)_4]^{6-}$ predominates. The instability constant of this complex may be determined from the equation:

$$\log K = \frac{E_X - E}{0.0295} + 4 \log a_{S_2O_3^{2-}} - \log 236 + \log C_{Hg^{2+}} \gamma_0 - \log C_{Hg^{2+}} \gamma_c \qquad (1)$$

where

E_X is the potential of the mercury electrode in the solution of complex salt measured against the saturated calomel electrode;

E is the potential in the absence of sodium thiosulfate at the same initial concentration of Hg^{2+} (in $2 \cdot 10^{-3}$ M solution, E = 0.4759 V);

$a_{S_2O_3^{2-}}$ – is the activity of the thiosulfate ion;

$C_{Hg^{2+}}$ is the initial concentration of divalent mercury ions;

$\gamma_0 \gamma_c$ are the activity coefficients of the simple and complex ions;

Since the activity coefficients of both the simple mercury ions and the complex mercury thiosulfate ions are unknown, calculation was performed by a simplified approximate equation in which we neglected the difference in the activity coefficients of the simple and complex ions.

In the calculations the equilibrium constant of the reaction $Hg^{2+} + Hg \rightleftharpoons Hg_2^{2+}$ was assumed to be 235 [9]

Values of the instability constants calculated from the above-mentioned equations are set forth in Table 3.

For determination of the consecutive instability constants and of the conditions of formation of the coordinatively unsaturated complexes we made use of Yatsimirsky's method [8].

The equilibrium activities of SO^{2-} were first calculated, applying the concept of the mean coordination number N introduced by Leden [10]. The approximate value of N was found from the graph obtained by plotting the potential of the mercury electrode (E_{Hg}) against the logarithm of the total activity of $S_2O_3^{2-}$ ($\log a_{total}$). In a certain narrow range of concentrations of $S_2O_3^{2-}$ it is possible to distinguish the rectilinear portions. The angular coefficient of these straight lengths must be.

$$\frac{dE}{d\log a_{total}} = \frac{N\cdot 0.0295\, a_{total}}{a_{total} - NC_{Hg^{2+}}} \quad (2)$$

We found the following values of the tangents of the angles of slope of three straight lines: 0.120, 0.127, 0.109. From equation (2) N was calculated for each concentration of $S_2O_3^{2-}$ and then, from the N values, the equilibrium activities of $S_2O_3^{2-}$ were determined.

A graph was then plotted from the above data (Figs. 1 and 2) from which, by Yatsimirsky's method, the consecutive instability constants of the thiosulfate complexes of mercury were determined.

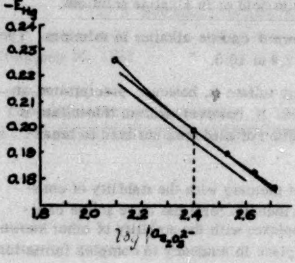

Fig. 1. Dependence of electrode potential on the logarithm of the activity of the complex-forming salt.
(Angular coefficient of tangent = 0.074).

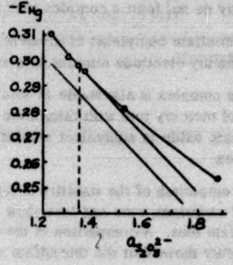

Fig. 2. Dependence of electrode potential on the logarithm of the activity of the complex-forming salt.
(Angular coefficient of tangent = 0.103).

The curve of Fig. 1 covers the region of sodium thiosulfate activities between $1.9\cdot 10^{-3}$ and $1.6\cdot 10^{-2}$ molar. The point of its contact with the straight line whose tangent of angle of slope is equal to 0.074 ($2.5\cdot 0.0295$) corresponds to a $S_2O_3^{2-}$ activity of $4\cdot 10^{-3}$ mole. This value is equal to the consecutive instability constant of $K_{3,2}$.

Fig. 2 was plotted from data obtained with higher activities of $S_2O_3^{2-}$ (from $1.3\cdot 10^{-2}$ to $6.8\cdot 10^{-2}$). In this case the tangent has an angular coefficient of 0.103 ($3.5\cdot 0.0295$). The point of contact corresponds to a logarithm of the activity of $Na_2S_2O_3$ equal to −1.324. Hence the consecutive instability constant $K_{4,3} = 4.5\cdot 10^{-2}$. We can now calculate the total instability constants of thiosulfate complexes of mercury:

$$K_3 = \frac{K_4}{K_{4,3}} = 5.5\cdot 10^{-33},$$

$$K_2 = \frac{K_3}{K_{3,2}} = 1.37\cdot 10^{-30}.$$

It is not difficult to determine the region of thiosulfate ion concentrations most favorable for existence of each complex. Evidently the complex ion $[Hg(S_2O_3)_2]^{2-}$ preponderates in a solution whose thiosulfate ion concentrations do not exceed $4\cdot 10^{-3}$ g-ions/l. In the region of sodium thiosulfate concentrations between $4\cdot 10^{-3}$ and $4.8\cdot 10^{-2}$ g-ions/l; the dominating complex group is $[Hg(S_2O_3)_3]^{4-}$. At higher sodium thiosulfate concentrations, a large proportion of the mercury ions are in the form of the complex $[Hg(S_2O_3)_4]^{6-}$.

TABLE 3

Activity of $Na_2S_2O_3$	$E_x - E$	K
$1.06 \cdot 10^{-1}$	−0.8093	$2.46 \cdot 10^{-34}$
$1.24 \cdot 10^{-1}$	−0.8179	$2.50 \cdot 10^{-34}$
$1.71 \cdot 10^{-1}$	− 0.8336	$2.46 \cdot 10^{-34}$

TABLE 4

Complex ion	Instability constant
$[Hg(S_2O_3)_4]^{6}$	$2.5 \cdot 10^{-34}$
$[Hg]_4^{2-}$	$5.2 \cdot 10^{-31}$
$[Hg(CNS)_4]^{2-}$	$1 \cdot 10^{-22}$
$[HgBr_4]^{2-}$	$2.3 \cdot 10^{-22}$
$[HgCl_4]^{2-}$	$1.2 \cdot 10^{-15}$

We were unable to detect the existence of a complex of mercury with one thiosulfate residue. When mercuric oxide or iodide reacts with thiosulfate ions, disappearance of turbidity is observed only when the sodium thiosulfate is added in quantity corresponding to the formation of $[Hg(S_2O_3)_2]^{2-}$ ions. This is also consistent with the data of potentiometric titration [3].

Formation of thiosulfate complexes is characteristic only of ions of divalent mercury. Ions of monovalent mercury do not form a complex with thiosulfate ions either in acid or in alkaline solutions.

Thiosulfate complexes of divalent mercury are stable toward caustic alkalies in solutions. The potential of the mercury electrode remains constant in the pH range of 7.9 to 10.3.

The complex is also stable in acidic solutions. Mercurous sulfate is, however, precipitated on direct interaction of mercury ions with thiosulfate ions in an acid medium. If, however, sodium thiosulfate is added to the mercuric oxide in equivalent amount, then subsequent addition of acid does not lead to breakdown of the complex.

A comparison of the stability of thiosulfate complexes of mercury with the stability of complex thiosulfates of cadmium, zinc and lead show that ions of divalent mercury form the more stable complexes with thiosulfate ions. A comparison of the stability of these complexes with the stability of other known complexes of mercury shows that the thiosulfate residue takes the first place in tendency to complex formation in a series of addends:

$$S_2O_3^{2-} - I^- - CNS^- - Br^- - Cl^-.$$

In Table 4 are set forth the values of the instability constants of some complexes of mercury.

A similar order of arrangement of addends is characteristic of the complexes also formed by other central ions [11, 12].

SUMMARY

1. A potentiometric investigation of thiosulfate complexes of mercury was undertaken.

2. It was shown that in aqueous solutions, ions of divalent mercury form complexes with different numbers of coordinative groups with the thiosulfate ion: $[Hg(S_2O_3)_2]^{2-}$, $[Hg(S_2O_3)_3]^{4-}$ and $[Hg(S_2O_3)_4]^{6-}$.

3. The instability constants of the complexes were calculated.

$$K_2 = 1.37 \cdot 10^{-30},\ K_3 = 5.5 \cdot 10^{-28},\ K_4 = 2.48 \cdot 10^{-34}.$$

4. Thiosulfate complexes of mercury are distinguished by high stability both in comparison with known thiosulfate complexes of other metals and in comparison with known complexes of mercury with other addends.

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* See Consultants Bureau Translation, p. 1461.

** See Consultants Bureau Translation, p. 239.

DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF THE SULFATES AND MOLYBDATES OF SODIUM AND SILVER IN MELTS

I. N. Belyaev and A. K. Doroshenko

In this paper are presented the results of an investigation by the visual-polythermal method of the surface of crystallization of the ternary reciprocal system Na, Ag ‖ SO_4, MoO_4, which belongs to a series of systems under investigation by one of the authors [1,2,3] involving sulfates and molybdates (tungstates) of alkali metals and metals giving ions with an 18 (Ag) or 18 + 2 (Tl, Pb) electron shell.

EXPERIMENTAL

The procedure has been described before [1,2]. The Na_2SO_4 and Na_2MoO_4 used were chemically pure grades with melting points of 884° and 688°, respectively; the Ag_2SO_4 was prepared by precipitation from $AgNO_3$ solution with sulfuric acid [4], and had m.p. 658°; the Ag_2MoO_4 was prepared by fusing $AgNO_3$ with MoO_3 in the stoichiometric ratio[5] and had m.p. 554°.

All percentages given in the paper are molar.

Binary Systems

The system silver sulfate – sodium sulfate has been studied by Nacken [6]; we made a fresh study of it. It forms continuous solid solutions (Fig. 1). We also repeated the examination of the system sodium molybdate – sodium sulfate, previously studied by Becke [6]. The system is characterized by the presence of a continuous series of solid solutions with a minimum at 673° and 25% Na_2SO_4 (Fig. 1). The system silver molybdate – silver sulfate (Table 1, Fig. 1) is here investigated for the first time. It was found to have a eutectic at 497° and 33% Ag_2SO_4. The system silver molybdate – sodium molybdate (Table 1, Fig. 1) is likewise here investigated for the first time. It is characterized by the presence of a continuous series of solid solutions with a minimum at 546° and 21% Na_2MoO_4.

Diagonal Sections

The silver molybdate – sodium sulfate section (Table 1, Fig. 1) has the form of a simple binary system with a eutectic at 547° and 5.5% Na_2SO_4. The character of the fusibility diagram indicates that this section is a stable diagonal section of the reciprocal system. The silver sulfate – sodium molybdate section (Table 1, Fig. 1) also consists of two crystallization branches and resembles the usual binary systems, but here the intersection of these branches is not eutectic in character, and the crystallization branch starting from Ag_2SO_4 first drops slightly, and then rises steeply to form a ridge of the stable solid solutions (Na, Ag)SO_4. Consequently, the section is not stable, since it intersects the field of the product of decomposition – sodium sulfate – with which silver sulfate forms a continuous series of solid solutions.

Internal Cuts

For clarification of the character of the interaction within the reciprocal system, the distributions of the lines of common crystallization and of the projection of the fields of crystallization of 15 internal cuts were studied in several directions. The fusion data for the cuts are set forth in Table 2 (Figs. 2 and 3). The fusibilities of the side lines, diagonal sections and a fairly large number of internal cuts permitted sufficiently accurate delineation of the surface of crystallization of the system (Fig. 4). The isotherms through 25° are plotted for a more informative representation of the surface of crystallization on the orthogonal projection (Fig. 4).

From Fig. 4 we see that the system studied belongs to the irreversible-reciprocal type [9] with a stable diagonal section of $Ag_2MoO_4 - Na_2SO_4$, although the deviation of the ridge from the stable diagonal and the course of the isotherms in the (Na, Ag)SO_4 field point to a certain reversibility of the reaction

$$Ag_2SO_4 + Na_2MoO_4 \rightleftharpoons Ag_2MoO_4 + Na_2SO_4.$$

The largest field of crystallization in the system belongs to the most stable solid solutions of (Na, Ag)SO_4, while the smallest field of crystallization belongs to the less stable solid solutions of (Na,Ag)MoO_4

TABLE 1

Lateral and Diagonal Sections

1st column—added component; 2nd column% of added component 3rd column—temp. of appearance of first crystals

1	2	3
$Ag_2MoO_4-Ag_2SO_4$		
Ag_2SO_4	0	554
	5	550
	10	541
	15	534
	20	524
	25	514
	30	505
	32.5	498
	35	500
	37.5	505
	40	509
	45	519
	50	526
	55	535
	60	544
	65	555
	70	564
	75	576
	80	590
	85	603
	90	620
	95	637
	100	658
$Ag_2MoO_4-Na_2MoO_4$		
Na_2MoO_4	0	554
	5	553
	10	550
	15	548
	17.5	547
	20	546
	22.5	546
	25	548
	27.5	550
Na_2MoO_4	30	553
	32.5	560
	35	566
	40	580
	45	597
	50	611
	55	622
	60	632
	65	640
	70	648
	75	656
	80	662
	85	668
	90	674
	95	681
	100	688
$Ag_2MoO_4-Na_2SO_4$		
Na_2SO_4	0	554
	2.5	550
	5	548
	7.5	587
	10	638
	15	692
	20	728
	25	753
	30	770
	35	779
	40	784
	45	787
	50	791
	55	794
	60	797
	65	801
Na_2SO_4	70	807
	75	815
	80	826
	85	839
	90	853
	95	869
	100	884
$Ag_2SO_4-Na_2MoO_4$		
Na_2MoO_4	0	658
	5	657
	10	659
	15	665
	20	674
	25	694
	30	720
	35	746
	40	769
	45	782
	50	791
	52.5	790
	55	786
	60	770
	65	740
	70	699
	72.5	676
	75	657
	77.5	647
	80	649
	82.5	652
	85	658
	90	668
	95	677
	100	688

The line of common crystallization, dividing the system into two parts, extends from the eutectic on the side line of $Ag_2SO_4-Ag_2MoO_4$ nearly to the side of $Na_2SO_4-Na_2MoO_4$. The close approach of the line of common crystallization to the $Na_2SO_4-Na_2MoO_4$ side points to the instability of solid solutions of $Na_2(MoO_4, SO_4)$ inside the reciprocal system and to their breakdown under the influence of the silver ion to form the more stable solid solutions of $(Ag, Na)SO_4$ and $(Na, Ag)MoO_4$.

Attention should be directed to the fact that in the binary systems $Na_2SO_4-Na_2MoO_4$ and $K_2SO_4-K_2MoO_4$ continuous series of solid solutions are formed, whereas in the systems $Ag_2SO_4-Ag_2MoO_4$ (studied by us) and $PbSO_4-PbMoO_4$ [6] a continuous series of solid solutions is not formed, just as chromates and molybdates of sodium and chromates and molybdates of potassium [6] form continuous series of solid solutions while in the system of lead chromate and molybdate there is limited solubility in the solid state with a eutectic.

It is interesting to compare the system Ag, Na ‖ SO_4, MoO_4 with the previously studied systems

TABLE 1

Summarized Data for the Internal Cuts: A) Na_2MoO_4, B) Ag_2MoO_4, C) Na_2SO_4, D) Ag_2SO_4, E) (Na, Ag)MoO_4, F) $Na_4(MoO_4, SO_4)$, G) (Na, Ag)SO_4.

No. of cut	Initial mixture in %	M.p. of starting mixture	Component added	Branches of crystallization curves: Branch 1	Intersection of branches 1 and 2: %	Intersection of branches 1 and 2: Temp.	Branch 2
I	87.5 A 12.5 B	670*	C	F	–	–	–
II	57.5 A 42.5 B	626		E	14	625*	G
III	42.5 A 57.5 B	589			3.5	587	
IV	25 A 75 B	548			1.5	546	
V	12.5 A 87.5 B	549			1.0	547	
VI	87.5 B 12.5 D	538			3.5	531	
VII	70 B 30 D	505			1.0	504	
VIII	62.5 B 37.5 D	505	A	G	63.0	624	E
IX	55 B 45 D	519	C		–	–	–
X	47.5 B 52.5 D	529	A		68.0	633	E
XI	35 B 65 D	555			71.0	637	
XII	15 B 85 D	603			74.0	643	
XIII	75 D 25 C	733			73.5	652	
XIV	50 D 50 C	791			70.5	658	
XV	25 D 75 C	832			66.5	665	

of Na, Pb ‖ SO_4, MoO_4 [1] and Na, Pb ‖ SO_4, WO_4 [2], in which the solid solutions of $Na_4(SO_4, MoO_4)$ and $Na_4(WO_4, SO_4)$ do not break down even inside the reciprocal systems. The very low stability of solid solution of $Na_4(MoO_4, SO_4)$ in the system Ag, Na ‖ SO_4, MoO_4 indicates a differing influence of the Ag and Pb ions upon the stability of the solid solutions. It is possible that this is associated with the presence in the system Na, Ag ‖ SO_4, MoO_4 of the more stable solid solutions of (Na, Ag)MoO_4, (Na, Ag)SO_4, in which the difference in the dimensions of the Na and Ag ions is considerably less than the difference between the SO_4'', MoO_4'' ions in systems [1,2], on the $Na_2SO_4-PbSO_4$ and $Na_2MoO_4-PbMoO_4$ sides of which there are no continuous series of solid solutions.

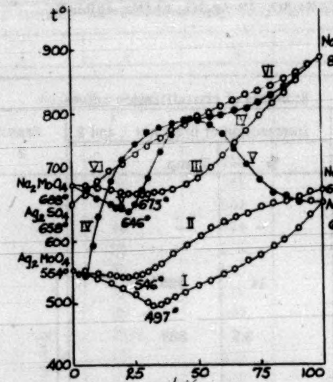

Fig. 1. Fusibility diagram.
I) B – G, II) B – A, III) A – C, IV) B – C, V) A – D, VI) D – C.
Explanation in text and Table 2.

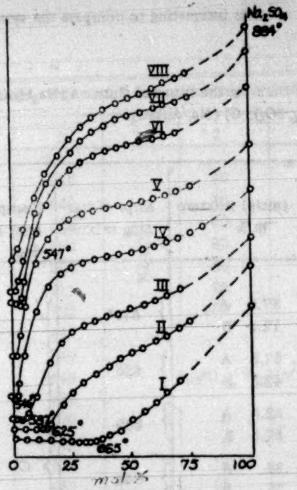

Fig. 2. Fusibility of sections through the reciprocal system.
Explanation in text and Table 2.

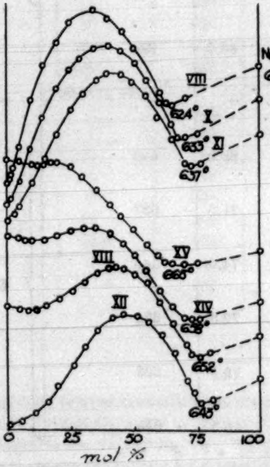

Fig. 3. Fusibility of sections through the reciprocal system
Explanation in text and Table 2.

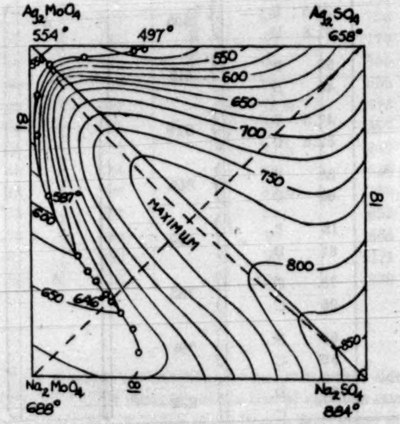
Ag_2MoO_4 554°
497°
Ag_2SO_4 658°
550
600
650
700
750
800
850
587°
600
650
646°
MAXIMUM
Na_2MoO_4 688°
Na_2SO_4 884°

Fig. 4. Orthogonal projection on to the square of compositions of the system Na, Ag ‖ SO_4, MoO_4

In the systems Na, Pb || SO_4, MoO_4 and Na, Pb || SO_4, WO_4 the equilibrium is shifted to the side of the pair of salts, one of which contains a cation with an 18 + 2 electron shell and an anion containing an element with an incomplete d-electron shell (W, Mo)–(Na_2SO_4–$PbWO_4$ and Na_2SO_4–$PbMoO_4$); in the system Ag, Na || MoO_4, SO_4 the equilibrium is displaced to the side of the pair of salts, one of which contains a cation with an 18-electron shell (Ag) and an anion containing an element with an incomplete d-electron shell (Mo). This enables us to state that, in general, in ternary reciprocal systems in which there is one cation with an 18 + 2 (Tl, Pb) or 18 (Ag) external electron shell, and in which one anion contains an element with an incomplete d-electron shell (Mo, W), the equilibrium is shifted in the direction of the pair of salts, one of which contains a cation with an 18- or 18 + 2-external electron shell and an anion with an incomplete d-shell ($PbMoO_4$, Pb WO_4, Ag_2MoO_4).

In the second of the two systems compared, the largest crystallization surface is possessed by $PbMoO_4$, $PbWO_4$; in the first, on the contrary, the largest surface belongs to Na_2SO_4; this inversion is in close harmony with the rules given in the literature [7, 8]. In arrangement and character of the fields of crystallization, the system here studied is similar to the system Na, Ag || Br, I [8].

SUMMARY

1. Using the visual-polythermal method, a study has been made for the first time of the binary systems Na_2MoO_4–Ag_2MoO_4 and Ag_2SO_4–Ag_2MoO_4. In the first are formed continuous solid solutions of (Na, Ag)MoO_4 with a minimum at 546° and 21% Na_2MoO_4, while the second gives a eutectic at 497° and 33% Ag_2SO_4.

2. The surface of crystallization of the ternary reciprocal system Na, Ag SO_4, MoO_4 was studied. It was shown that the system belongs to the irreversible-reciprocal type with the stable diagonal section of Na_2SO_4–Ag_2MoO_4.

3. It was established that inside the reciprocal systems the silver ion has a considerably greater influence on the stability of solid solutions of $Na_2(MoO_4, SO_4)$, than the lead ion.

4. The hypothesis is advanced that in ternary reciprocal systems with participation of one cation with an 18- or 18 + 2- external electron shell and one anion containing an element with an incomplete d-electron shell, the equilibrium is shifted in the direction of the pair of salts, one of which also contains a cation with an 18- or 18 + 2- electron shell and an anion containing an element with an incomplete d-electron shell.

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PREPARATION OF PURE VANADYL CHLORIDE SOLUTION

V. L. Zolotavin

A method is described in the literature [1] for the preparation of solutions of vanadyl sulfate and vanadyl chloride by the action of metallic mercury on an acidified solution of ammonium vanadate. Removal from the solution of ions of the resultant univalent mercury is effected by adding – in the case of sulfate solutions – potassium chloride or sodium chloride in quantity slightly in excess of the calculated quantity. These processes may be expressed by the following equations:

$$2HVO_3 + 2Hg + 3H_2SO_4 = 2VOSO_4 + Hg_2SO_4 + 4H_2O;$$

$$2HVO_3 + 2Hg + 6HCl = 2VOCl_2 + Hg_2Cl_2 + 4H_2O.$$

Actually, from a comparison of the normal oxidation-reduction potentials of the two systems:

$$E_0 VO^{2+} + 3H_2O \mid V(OH)_4^+ + 2H^+ = 1V \text{ and } E_0 2Hg + 2Cl^- \mid Hg_2Cl_2 = 0.2627 \text{ V},$$

we see clearly that the reduction of vanadium from the quinquevalent to the quadrivalent state proceeds almost completely under the action of metallic mercury in presence of chlorine ions.

The method proposed by the authors cited, however, is not free from defects: use of ammonium vanadate as starting material is bound to lead to the introduction of ammonium ions into the solution of vanadium salt. Moreover, when preparing a solution of vanadyl sulfate, the presence of potassium or sodium ions is inevitable, as is also a small quantity of chlorine ions.

We used* freshly precipitated vanadium pentoxide as starting material with the objective of eliminating these defects and obtaining a pure solution of vanadyl chloride. To a hot, nearly saturated ammonium vanadate solution containing about 50 g salt in 900 ml water was added 100 ml dilute hydrochloric acid (1:3). The precipitated V_2O_5 was filtered off and washed with hot water acidified with hydrochloric acid.

A pure vanadyl chloride solution was prepared by adding to a beaker, containing hydrochloric acid solution of a definite concentration, vanadium pentoxide in quantity determined from the required content of vanadyl ion in the solution; metallic mercury was added in excess and the mixture was agitated for 5-10 minutes. After filtering off the precipitate of residual mercury and of the calomel formed, a pure solution of vanadyl chloride was obtained.

Complete reduction of the vanadium to the quadrivalent form was effected by the following procedure: 25 ml of the obtained solution was pipeted off and 10 ml H_2SO_4 and 10 ml Reinhardt mixture were added to it; the mixture was heated to 60° and titrated with potassium permanganate to a pink color which persisted for 1 minute.

To another equal portion of the solution was added 10 ml H_2SO_4 and a stream of sulfur dioxide was passed through while heating on a water bath; the excess of sulfur dioxide was eliminated by passing carbon dioxide (test by cessation of decolorization of acidified permanganate solution with the evolved gas). After 10 ml Reinhardt mixture ha had been added, titration was performed with permanganate. The good reproducibility of the results showed that the metallic mercury had substantially reduced VO_3^- to VO^{2+}.

Expt. No.	Amount of V_2O_5 suspension (in ml)	Normality of HCl	$KMnO_4$ consumed in titration (in ml)	
			after reduction of Hg	after supplementary reduction with SO_2
1	2	0.5	2.20	2.30
2	2	0.1	2.40	2.46
3	5	0.1	6.15	6.10
4	5	0.1	6.95	6.95
5	10	0.05	4.80	4.85
6	10	0.05	4.60	4.66

Note: The difference between experiments 1-2, 3-4 and 5-6 is accounted for by the difference in V_2O_5 content of the suspension.

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* A. A. Ryzh participated in the experimental work.

All these experiments were carried out with 1 N hydrochloric acid. Desiring to obtain vanadyl chloride solutions of lower acidity, we prepared a suspension of vanadium pentoxide in solutions of hydrochloric acid of the following concentrations: 0.5, 0.1, 0.05 and 0.01 N. Experimental results are set forth in the table.

The data show that substantially complete reduction of vanadium by mercury is effected even in 0.05 N HCl. When using 0.01 N solution, however, the absence of complete reduction was evident from the color of the solution. This is undoubtedly a defect of the method.

SUMMARY

1. An improved method is proposed for the preparation of pure solutions of vanadyl chloride by reduction of freshly precipitated vanadium pentoxide with metallic mercury.

2. It was established that the lowest acidity that can be attained is 0.05 N.

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CRACKING OF NORMAL PARAFFINIC HYDROCARBONS IN PRESENCE OF ALUMINUM CHLORIDE

II. CRACKING OF n-HEXADECANE

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The cracking of low-molecular normal paraffinic hydrocarbons (from C_5 to C_8) in presence of aluminum chloride has been extensively studied in numerous investigations. The cracking of normal paraffinic hydrocarbons of higher molecular weights has hardly been studied. Only some isolated papers have been published and we have previously drawn attention to them [1]. Gault and Sigwalt [2] have described the cracking of n-hexadiene in presence of $AlCl_3$. They obtained propane, butane and higher boiling hydrocarbons which were not investigated in detail. Bauer and Toma [3] cracked octadecane and hexatriacontane in presence of 25% $AlCl_3$ and obtained low-molecular paraffinic hydrocarbons about whose structure no information was given.

In the present investigation, n-hexadecane* was cracked in the apparatus which we previously described at atmospheric pressure in presence of HCl in the temperature range of 150-250°, using 5 to 15% $AlCl_3$. The temperature in the glass-packed column was maintained at 110-120°.

The composition and yield of gaseous products of cracking of n-hexadecane are set forth in Table 1.

TABLE 1

Composition and Yield of Gaseous Products of Cracking of n-Hexadecane in Presence of $AlCl_3$ (in weight %)

Conditions	Number of experiment				
	1	2	3	4	5
Temperature	100	150	200	200	250
Weight percentage of $AlCl_3$	15	15	15	7.5	5
Duration in hours	8	8	4	6	9
Extent of conversion	53.8	58.5	100	73.5	73.9
Composition of gas:					
H_2	Traces	Traces	Traces	Traces	Traces
CH_4	1.2	0.7	0.7	1.5	Traces
C_2H_6	0.4	0.0	0.1	0.8	0.0
C_3H_8	0.5	2.5	6.0	2.2	9.1
iso-C_4H_{10}	96.0	96.8	93.2	95.5	88.6
n-C_4H_{10}	1.9	0.0	0.0	0.0	2.3
Yield of gas:					
on the original n-hexadecane	15.0	19.4	33.4	25.0	24.2
on the reacted n-hexadecane	27.9	33.1	33.4	34.0	32.8

The main component of the gas, as in the case of cracking of n-heptane and n-nonane, is isobutane. The gases resulting from the cracking of hexadecane contain, however, a larger amount of propane (up to 9 wt.-% of the gas). The yield of propane, as in the case of cracking of n-heptane and n-nonane, increases with the cracking temperature (Experiments 1, 2, 3, 5). An increase in the quantity of $AlCl_3$ introduced into the reaction also increases the yield of propane (Expts. 3 and 4).

The material balance of the products of cracking of n-hexadecane is given in Table 2, which indicates that the main bulk of the liquid products of cracking boils up to 100°. Hydrocarbons boiling at higher temperatures are obtained in low yields (1.3-3.8% reckoned on the original hydrocarbon).

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* n-Hexadecane was obtained by recrystallization of standard cetane [4]. The initial temperature of crystallization was 17.85°; b.p. 286°; d_4^{20} 0.7735; n_D^{20} 1.4350.

TABLE 2

Yield of Products of Cracking of n-Hexadecane in Presence of $AlCl_3$ (in percentages by weight)

Conditions	Number of experiment				
	1	2	3*	4	5
Temperature	150°	200°	200°	200°	250°
Weight-% $AlCl_3$	15	15	10	7.5	5
Duration (in hours)	8	4	16	6	9
Gas	19.4	33.4	14.9	25.0	24.2
Including:					
iso-C_4H_{10}	18.8	31.2	–	23.9	21.4
Fractions:					
27-29°	10.5	19.1	10.3	14.6	14.6
29-38°	1.1	0.5	0.3	0.2	0.4
38-64°	6.9	12.8	7.9	10.2	10.5
64-77°	0.8	1.2	0.9	1.1	0.8
77-94°	0.7	6.9	4.6	5.2	4.5
94-100°	0.5	1.0	3.8***	0.3	–
100-120°	–	2.7	–	0.6**	1.3
120-284°	1.5	–	–	2.4	0.5
284-286°	41.4	–	46.6	26.5	26.1
Hydrocarbons combined with $AlCl_3$ in residue after cracking	17.2	22.4	10.7	13.9	17.1
Total percentage decomposition of original hydrocarbon	58.6	100.0	53.4	73.5	73.9

After 8 hours at 150°, n-hexadecane is only converted to the extent of 58.6%. When the temperature is raised to 200° (Expt. 2) it is completely cracked in 4 hours. Reduction of the quantity of $AlCl_3$ from 15 to 7.5% (Expt. 4) lowers the conversion after 6 hours to 73.5%. Attainment of the same percentage decomposition as in Expt. 4 when using 5% $AlCl_3$ (Expt. 5) requires a rise of temperature to 250° and a reaction duration of 9 hours.

TABLE 3

Hydrocarbon Composition of Fractions Obtained by Cracking of n-Hexadecane, determined by the Raman method****

Hydrocarbon composition (in percentages by wt.)	Number of experiment					
	2		4			1, 2, 3, 4, 5
	Boiling limits of fractions (in °)					
	38-64	77-94	27-38	38-64	77-94	64-77*****
Isopentane	–	–	100	–	–	–
n-Pentane	–	–	–	–	–	–
2-Methylpentane	60	–	–	70	–	–
3-Methylpentane	12	–	–	20	–	30
2,2-Dimethylbutane	3	–	–	–	–	–
2,3-Dimethylbutane	15	–	–	–	–	–
n-Hexane	10	–	–	10	–	13
2-Methylhexane	–	50	–	–	35	–
3-Methylhexane	–	22	–	–	20	–
2,4-Dimethylpentane	–	20	–	–	13	50
2,3-Dimethylpentane	–	–	–	–	27	–
2,2,3-Trimethylbutane	–	8	–	–	5	7

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* Experiment in absence of HCl

** Fraction 100-107°.

*** Fraction 94-284°.

**** The analysis was carried out in the laboratory of molecular spectroscopy of Moscow State University under the direction of V. M. Tatevsky.

***** The 64-77° fractions from these experiments were combined.

Introduction of hydrogen chloride into the reaction zone considerably speeds up the cracking reaction in presence of $AlCl_3$; thus, in presence of HCl (1-1.1%) and 7.5% $AlCl_3$ with a duration of experiment of 6 hours, the percentage conversion is 73.5; in the absence of HCl and using 10% $AlCl_3$, the n-hexadecane is only 53.4% converted after 16 hours.

The chemical composition of the liquid products of cracking of n-hexadecane, boiling up to 100°, is determined on the basis of data for fine rectification, for the physical constants of the fractions* and for the Raman spectra (Table 3). Their main components are isopentane, isohexanes and isoheptanes, i.e., the same products as in the case of cracking of n-heptane and n-nonane [1].

The pentane fraction is pure isopentane; n-pentane was found in traces. The main component of the isohexane fraction is 2-methylpentane; that of the isoheptane fraction is 2-methylhexane. Very much smaller amounts of isomers with the methyl group in the 3-position are formed (up to 20% of the fraction); the same is true of isomers with 2-methyl groups in the 2,3- and 2,4-positions (up to 15%). Hydrocarbons containing a quaternary carbon atom are formed in still smaller quantity (from 3% to 8% on the fraction).

Independently of the experimental conditions, the yield of the main components of the products of cracking of n-hexadecane are in decreasing order from isobutane to isopentane (Table 4).

TABLE 4

Yield of Isoparaffinic Hydrocarbons in Cracking of n-Hexadecane (in percentages by weight of the reacted hydrocarbon)

Expt. No.	Conditions of experiment			Degree of conversion	Isobutane	Isopentane	Isohexanes	Isoheptanes
	Temp.	$AlCl_3$ (in wt.-%)	duration (in hrs.)					
1	150°	15	8	58.6	32.2	19.7	11.1	2.1
2	200	15	4	100	31.2	19.6	11.9	7.6
3**	200	10	16	53.4	–	19.8	13.8	9.5
4	200	7.5	6	73.5	32.4	20.2	12.8	7.8
5	250	5	9	73.9	29.0	20.3	13.1	6.7

TABLE 5

Characterization of Products of Cracking of n-Hexadecane Boiling above 100°

Expt. No.	Expt. conditions			Boiling range of fractions	d_4^{20}		n_D^{20}		Critical temp. of solution in aniline after sulfonation *****	Hydrocarbon sulfonated (in wt.-%)	Specific dispersion
	temperature	$AlCl_3$ (in wt.-%)	duration (hrs.)		before sulfonation	after sulfonation	before sulfonation	after sulfonation			
6	200°	15	4	100-120°****	0.7072	0.7066	1.3989	1.3990	71.7°	0.5	–
3***	200	10	16	207-284	0.7942	0.7935	1.4418	1.4400	89.2	2.0	100.5
4	200	7.5	6	100-107	0.7000	–	1.3960	–	–	–	–
4	200	7.5	6	107-246	0.7957	0.7930	1.4400	–	71.7	7.0	–
4	200	7.5	6	246-284	0.7848	0.7840	1.4371	1.4373	91.6	5.0	–
7	100	15	8	129-284	0.7872	–	1.4400	–	–	–	100.4
1	150	15	8	100-284	0.8542	–	1.4638	–	–	–	100.8
2	200	15	4	100-125	0.7208	–	1.4065	–	–	–	–

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* Fractions: 1) 27-38°: d_4^{20} 0.6190-0.6195, n_D^{20} 1.3537-1.3539;
2) 38-64°: d_4^{20} 0.6551-0.6557, n_D^{20} 1.3727-1.3734;
3) 64-77°: d_4^{20} 0.6697-0.6707, n_D^{20} 1.3805-1.3810;
4) 77-94°: d_4^{20} 0.6831-0.6842, n_D^{20} 1.3872-1.3880.

** Experiment in absence of HCl.

*** Experiment in absence of HCl.

**** Residue after rectification (boiling range determined by distillation of residue from a Würtz flask of 5 ml capacity).

***** Sulfonation carried out with three volumes of 98% H_2SO_4.

The data of Table 4 show that in the temperature range 200-250° the yields of the main components of the products of cracking remain nearly constant when calculated on the reacted hydrocarbon. It would, therefore, appear that in this temperature range, the quantity of $AlCl_3$ and the presence of HCl are factors that only govern the velocity of the cracking reaction, but not the composition of final products.

Investigation of the products boiling above 100°, formed by cracking of n-hexadecane, showed that they are paraffinic hydrocarbons (Table 5) and similar in chemical composition to the high-boiling products of cracking of n-heptane and n-nonane [1].

An examination was also made of the hydrocarbons isolated from the residues obtained in the cracking of n-heptane, n-nonane and n-hexadecane in presence of $AlCl_3$. The isolation of these hydrocarbons, chemically combined with the $AlCl_3$ in the process of cracking, was effected by decomposing the residues with water in an atmosphere of carbon dioxide while cooling with ice.

The hydrocarbons separated in this manner from residues formed at experimental temperatures of 50 to 150° were dark oils, while the product formed at 200-250° (in the case of n-hexadecane) was a hard, powdery substance.

The isolated liquid hydrocarbons were dissolved in benzene and the solvent was distilled off at reduced pressure (residual pressure 30-35mm). The solid hydrocarbons (the pulverulent material) were transferred to a filter, washed with water until neutral and dried in a current of carbon dioxide. Results are set forth in Table 6. The remarkably high iodine numbers (222-306) and empirical formulas, calculated on the basis of the elementary composition and molecular weight), show that the bottom layer of cracked products contains highly unsaturated and polycyclic hydrocarbons.

TABLE 6

Characterization of Hydrocarbon Portion of Residues after Cracking of n-Paraffinic Hydrocarbons in Presence of $AlCl_3$ for 8 hours

Starting hydrocarbon	Experimental conditions		Molecular weight *	Iodine number**	Elementary composition (%)		Empirical formula
	temp.	$AlCl_3$ (wt.-%)			H	C	
n-Heptane	100°	20	305	302	11.23	88.54	$C_{22}H_{34}(C_nH_{2n-10})$
	50	10	287	302	12.00	87.25	$C_{21}H_{34}(C_nH_{2n-8})$
	100	10	298	292	11.63	88.23	$C_{22}H_{35}(C_nH_{2n-9})$
n-Nonane	150	10	308	306	10.47	88.86	$C_{23}H_{32}(C_nH_{2n-14})$
n-Hexadecane	100	15	301	221	11.55	88.31	$C_{21}H_{33}(C_nH_{2n-9})$
	150	15	347	253	10.0	89.39	$C_{26}H_{34}(C_nH_{2n-18})$

Unsaturated hydrocarbons are not present among the products of cracking of n-paraffinic hydrocarbons found in the upper layer. Formation on the one hand of saturated hydrocarbons and on the other hand of hydrocarbons with an extremely low hydrogen content (in the lower layer) must have involved a process of hydrogen rearrangement in which a portion of the hydrocarbons (low-molecular) becomes saturated with hydrogen at the expense of dehydrogenation of the high-molecular portion. This reaction is characteristic not only of the cracking of n-paraffinic hydrocarbons in presence of HCl but also of the cracking of other classes of hydrocarbons in presence of various catalysts [5, 6, 7]. Rise of cracking temperature and an increased amount of $AlCl_3$ lead to diminution of the hydrogen content of the hydrocarbon residue.

SUMMARY

1. The main products of cracking of n-hexadecane in presence of $AlCl_3$ are isoparaffinic hydrocarbons. Their yields fall off from isobutane to isoheptane regardless of the experimental conditions. Isomers with a methyl group in the 2-position are predominantly formed; those with a methyl group in the 3-position and with two methyl groups are formed in smaller quantities. Isomers with a quaternary carbon atom are also formed in small amount.

Low molecular paraffins of normal structure are formed in insignificant amounts.

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* By cryoscopic method.

** By Hübl -Waller method.

2. The gaseous products of cracking consist mainly of isobutane (88-96%); the yield of propane (on the total gas) reaches 9%. The propane yield increases with rising experimental temperature and with increasing amount of $AlCl_3$. Methane and ethane are formed in very minor amounts (0.7-2.3%).

3. Hydrocarbons boiling above 100° are formed in small amounts (up to 4%); they are paraffins.

4. The quantity of $AlCl_3$ and the presence of HCl in the 200-250° temperature range do not affect the composition of the final products of cracking of n-hexadecane, but they govern the reaction velocity.

5. The hydrocarbons isolated from the residues of cracking of n-heptane, n-nonane and n-hexadecane in presence of $AlCl_3$ are highly unsaturated compounds.

6. The similarity in composition of theproducts of cracking of n-heptane, n-nonane and n-hexadecane in presence of $AlCl_3$ testifies to the similarity of the mechanism of decomposition of normal paraffinic hydrocarbons of differing molecular weight in the conditions studied.

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* See Consultants Bureau Translation, page 225.

3. The various products of cracking [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] Methane and ethane are formed [illegible]

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THE HYDROGEN BOND AND THE PHYSICAL PROPERTIES OF SOME SUBSTITUTED PHENOLS AND ANISOLES

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Formation of a hydrogen bond in a molecule or between molecules leads to a marked change in their properties. Characteristics of these changes for infra-red and Raman spectra [1], for absorption in the ultraviolet and in the visible spectrum [2], and for the dipole moments of molecules [3] have been established. The data for different molecules, however, lead to conflicting conclusions regarding the character of the association of some substituted phenols and anisoles, in particular pyrocatechol, guaiacol and o-anisidine.

Pyrocatechol, for example, unlike other compounds with an intramolecular hydrogen bond, exhibits intense absorption in the region of the first harmonic and fundamental vibration frequencies of the isolated OH group [4] and absorbs in a shorter wave region of the ultraviolet than its para-isomer [5]. Data for the dipole moments [6] and some chemical properties of pyrocatechol [7] point to great stability of its intramolecular hydrogen bond. Similarly in the case of guaiacol the infra-red spectrum exhibits intense absorption in the region of vibration frequencies of the isolated OH group [4, 8]. Results of measurements of the dipole moments [9], however, led to the conclusion that the guaiacol molecule contains an intramolecular bond whose stability is even higher than that of o-hydroxyacetophenone.

Evidently, the data for the various properties of the molecules of the above-mentioned substances do not allow of a definite answer to the question of the character and stability of their association. Since for compounds with inter- and intramolecular hydrogen bonds a series of characteristics of their physical properties have been established (boiling point [10], density, surface tension and viscosity in the liquid state [11]), it is natural to compare the physical properties of dihydroxybenzenes and their ethers with the aim of determining the character and stability of the association in pyrocatechol and guaiacol. In Table 1, are set for the results of measurments of the density, viscosity and surface tension of these compounds in the liquid state at two temperatures (131 and 184°); data are also given for their boiling points.

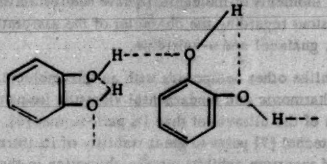
TABLE 1

Physical Properties of Dihydroxybenzenes and Their Ethers

Compound		Density at		Surface tension at		Viscosity $(\eta \cdot 10^3)$		B.p. at 760 mm
		131°	184°	131°	184°	131°	184°	
Dihydroxybenzene:	o-	1.137	1.071	36.5	32.0	18.09	8.41	245°
	m-	1,165	1,110	45,4	41,6	46.39	15,73	276
	p-	–	–	–	–	–	–	286
Methoxyphenol:	o-	1,022	0,953	28.8	23,8	6.43	3.97	205
	m-	1.052	0,990	33.6	29,3	–	5,36	244
	p-	1.060	0,999	34.2	29.9	13,44	6.88	243
Dimethoxybenzene:	o-	0,981	0.908	26.0	22.6	5.46	3,53	207
	m-	0,965	0.902	25,9	21,9	6.82	4.19	215
	p-	0,972	0,904	26,3	21.7	5.09	3,40	212

It follows from the above data that guaiacol, like all compounds with an intramolecular hydrogen bond, possesses exceptionally low values of all the properties enumerated in comparison with those of the isomers; in the case of the dimethyl ether, the lowering of the constants is much less marked than in the isomers (there is even a rise of boiling points); in contrast to the isomers, guaiacol possesses a lower surface tension and viscosity than the original phenol (at 131°, the surface tension of phenol is 30.0 erg/cm^2, the viscosity is $7.25 \cdot 10^3$ poises); compared with anisole, there is a rise of density almost identical with the increase of molecular weight, whereas in the isomers as in all intermolecularly associated compounds, the rise of density exceeds the increase of molecular weight. Hence, guaiacol both at 131° and 184° behaves like a compound with an intramolecular hydrogen bond. This also follows from the fact that it differs from its isomers in possessing a lower boiling point than its isolog — thioguaiacol; it also has an appreciably lower density and boiling point than its metamer — homopyrocatechol. A portion of the guaiacol molecules are evidently, nevertheless, intermolecularly associated, for in the series of isoperiodic compounds (compounds differing from one another not only in the number of hydrogen atoms, but also in containing atoms of elements in the same period of the periodic system) guaiacol deviates slightly in b.p. and other properties from the value corresponding to its dipole moment.

Pyrocatechol, likewise, manifests some of the above-mentioned features which are characteristic of compounds with an intramolecular hydrogen bond. Thus, it possesses appreciably lower values of all the above properties in comparison with resorcinol; unlike the latter it differs from phenol in the absence of an increasing density with rising molecular weight. In addition, however, pyrocatechol also manifests qualities characteristic of compounds which are intermolecularly associated through hydrogen bonds. Thus, in comparison with its monomethyl ether it possesses much higher values of all constants than does thiopyrocatechol; unlike guaiacol and the similarly intermolecularly associated cresols and benzyl alcohol, pyrocatechol has an anomalously high boiling point in the series of isoperiodic compounds (Fig. 2). Pyrocatechol must evidently be classed with the compounds which in the liquid state are of the mixed-associated type, i.e., both inter- and intramolecularly associated:



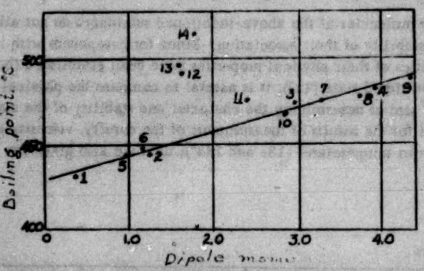


Fig. 1. 1) $C_6H_5C_3H_7$; 2) $C_6H_5OC_2H_5$; 3) $C_6H_5COCH_3$; 4) $C_6H_5NO_2$; 5) $C_6H_4(CH_3)OCH_3$-o; 6) $C_6H_4(CH_3)OCH_3$-p; 7) $C_6H_4(CHO)CH_3$-p; 8) $C_6H_4(CN)CH_3$-o; 9) $C_6H_4(CN)CH_3$-p, 10) $C_6H_4(CHO)OH$-o; 11) $C_6H_4(OCH_3)OH$-o; 12) $C_6H_5CH_2CH_2OH$; 13) $C_6H_4(OCH_3)NH_2$-o; 14) $C_6H_4(OCH_3)NH_2$-p.

TABLE 2

Physical Properties of Anisidines at 131°

Compound	Density d_4^{131}	Surface tension (ergs/cm²)	Viscosity ($\eta \cdot 10^3$)
Anisidine:			
o-	0.996	31.3	7.17
m-	0.997	33.0	–
p-	1.003	33.7	8.42

In Table 2 are set forth the results of measurements of density, viscosity and surface tension at 131° of o-, m- and p-anisidines.

It follows from the data that o-anisidine at 131° differs from pyrocatechol and guaiacol in behaving like a compound which does not possess an intramolecular hydrogen bond. An examination of the literature data for density and viscosity of o- and p-anisidines at 55° [12] and their density at 90° [13], nevertheless, offers evidence that at low temperatures the amino group in o-anisidine forms a hydrogen bond with the neighboring methoxy group. This bond, however, appears to be thermally unstable and is readily broken by heating with consequent appreciable reduction of the difference in the physical constants of the isomers at 131°. At this temperature, o-anisidine resembles its isomers in behaving like an intermolecularly associated compound. This also follows from the extent of depression of the boiling point of o-anisidine, as well as of its isomers, on conversion to the corresponding dimethylamino derivatives; there is a sharp deviation of the boiling point, surface tension and viscosity in the series of isoperiodic compounds from the straight line expressing the values of the constants as a function of the dipole moment (Figs. 1, 3, and 4).

EXPERIMENTAL

The methoxyphenols and dimethoxybenzenes were prepared by methylation of the respective hydroxy compounds with methyl iodide [14]. The anisidines were prepared by reduction of the corresponding methoxynitrobenzenes with zinc dust and HCl in alcoholic solution [15]. p-Anisidine was purified by recrystallization from water; pyrocatechol and resorcinol were purified by recrystallization from benzene; the remaining compounds were purified by three vacuum distillations.

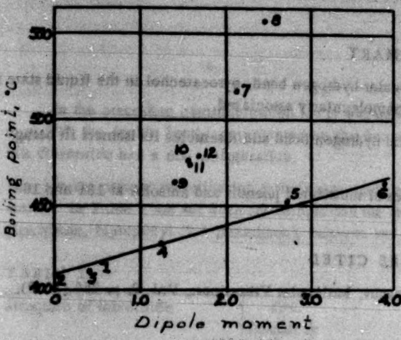


Fig. 2. 1) $C_6H_4(CH_3)_2$-o; 2) $C_6H_4(CH_3)_2$-p; 3) $C_6H_4(CH_3)_2$-m; 4) $C_6H_5OCH_3$; 5) C_6H_5CHO; 6) C_6H_5CN; 7) $C_6H_4(OH)_2$-o; 8) $C_6H_4(OH)_2$-p; 9) $C_6H_4(OH)CH_3$-o; 10) $C_6H_4(OH)CH_3$-m; 11) $C_6H_4(OH)CH_3$-p; 12) $C_6H_5CH_2OH$.

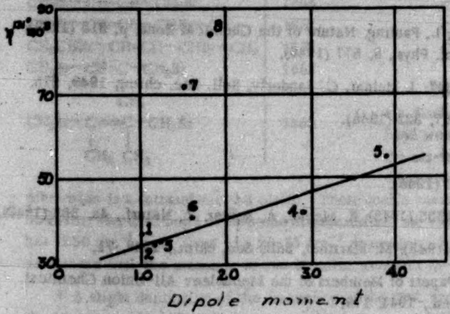


Fig. 3. 1) $C_6H_4(OCH_3)CH_3$-o; 2) $C_6H_4(OCH_3)CH_3$-m; 3) $C_6H_4(OCH_3)CH_3$-p; 4) $C_6H_5COCH_3$; 5) $C_6H_5NO_2$; 6) $C_6H_5N(CH_3)_2$; 7) $C_6H_4(NH_2)OCH_3$-o; 8) $C_6H_4(NH_2)OCH_3$-p.

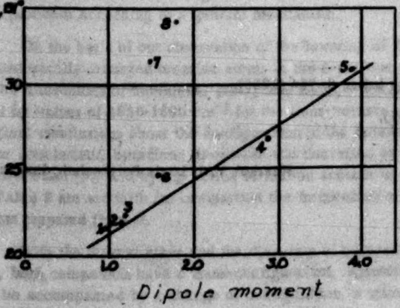


Fig. 4. 1) $C_6H_4(OCH_3)CH_3$-o; 2) $C_6H_4(OCH_3)CH_3$-m; 3) $C_6H_4(OCH_3)CH_3$-p; 4) $C_6H_5COCH_3$; 5) $C_6H_5NO_2$; 6) $C_6H_5N(CH_3)_2$; 7) $C_6H_4(NH_2)OCH_3$-o; 8) $C_6H_4(NH_2)OCH_3$-p.

The procedures for determination of density, viscosity and surface tension have been described previously.

All determinations were carried out in a steam thermostat [16]. The values of the constants of the hydroxy- and methoxy-substituted benzenes were generally in good agreement with the literature data [8, 17]. The values of the surface tension of pyrocatechol, resorcinol, p-methoxyphenol and m-anisidine are here given for the first time.

SUMMARY

1. Guaiacol in the liquid state possesses an intramolecular hydrogen bond; pyrocatechol in the liquid state is a mixed-associated compound, i.e., it is both inter- and intramolecularly associated.

2. o-Anisidine at 131° does not form an intramolecular hydrogen bond and resembles its isomers in being intermolecularly associated.

3. Densities, viscosities and surface tensions of a series of substituted phenols and anisoles at 131 and 184° were determined.

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* See Consultants Bureau Translation, page 589.

THE DIBROMIDES OF BUTADIENE AND ITS HOMOLOGS

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In the preceding communication [1] it was shown that in the Raman spectrum of the butadiene dibromide with m.p. 53°, the double bond is represented by the frequency of 1655 cm^{-1}, and on this was based the assumption that this dibromide had a cis-configuration.

In the present investigation a study was made of the Raman spectra of the dibromides of a series of conjugated dienes. In Table 1 are set forth for comparison the frequencies of the C=C bond of the dibromides of butadiene, piperylene, bipropenyl (2,4-hexadiene), isoprene and diisopropenyl (i.e., 2,3-dimethyl-1,3-butadiene).

TABLE 1

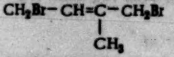
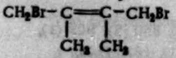
Structure of dibromide	C=C frequency (in cm^{-1})
$CH_2Br-CH=CH-CH_2Br$	1655
$CH_2Br-CH=CH-CHBr-CH_3$	1657
$CH_3CHBr-CH=CH-CHBr-CH_3$	1659
 $CH_2Br-CH=\underset{\underset{CH_3}{\vert}}{C}-CH_2Br$	1655
 $CH_2Br-\underset{\underset{CH_3}{\vert}}{C}=\underset{\underset{CH_3}{\vert}}{C}-CH_2Br$	1650

TABLE 2

Substance	C=C frequency (in cm^{-1})
$CH_2Br-CH=CH-CH_2Br$	1655
$C_2H_5OCH_2-CH=CH-CH_2OC_2H_5$	1677
$CH_3COOCH_2-CH=CH-CH_2OCOCH_3$	1677

The dibromides of butadiene, piperylene and 2,4-hexadiene are disubstituted ethylenes. It was to be expected that their double bond would be characterized by a frequency of 1655-1660 cm^{-1} for the cis-form and by 1670-1680 cm^{-1} for the trans form. Isoprene dibromide is a trisubstituted olefin while 2,3-dimethyl-1,3-butadiene dibromide is a tetrasubstituted olefin. Their double bond should have the frequency of 1675-1680 cm^{-1}. Actually, however, the C=C bond of isoprene dibromide has the value of 1655 cm^{-1}, and 2,3-dimethyl-1,3-butadiene dibromide has 1650 cm^{-1}, i.e., there is a 20-25 cm^{-1} depression of the frequency of the double bond. This depression may be associated with the presence of two bromine atoms in the β-position to the double bond.

A slight depression of the frequency of the C=C bond by the bromine atom in the β-position has been noted in the literature [2]. Thus, in propylene the frequency of the C=C bond is 1648 cm^{-1}, whereas in allyl bromide it is 1638 cm^{-1}.

From the Raman spectrographic data, we can conclude that the addition of bromine to butadiene and its homologs proceeds according to a general mechanism.

On the basis of our observation of the lowering of the frequency of the C=C bond under the influence of two symmetrically arranged bromine atoms in the β-position to the double bond by 20-25 cm^{-1}, it may be assumed that in the dibromides of butadiene, piperylene and 2,4-hexadiene, the frequency of the C=C bond should be characterized by values of 1650-1660 cm^{-1} for the trans-isomers and of 1630-1640 cm^{-1} for cis-isomers. Consequently, our original conclusions about the configuration of the butadiene dibromides require greater precision. In order to check these conclusions, butadiene dibromide was converted by treatment with sodium ethoxide into 2-butene-1,4-diol diethyl ether [3], and by the action of sodium acetate in acetic anhydride into the diacetate of the same glycol [4]. In Table 2 are set forth for comparison the frequencies of the C=C bond of the dibromide of butadiene and of the ethers prepared from it.

Both the diethyl ether and the diacetate of butenediol are characterized by a C=C frequency of 1677 cm^{-1}, i.e., both compounds have a trans-configuration. Assuming that substitution of bromine by ether or ester groups should not be accompanied by a change of configuration, a trans-configuration must also be assumed for the original butadiene dibromide.

These data are in harmony with recently published results of an investigation of butadiene dibromide [5], which established that the infra-red spectrum contains an absorption maximum at 10.3μ, which is characteristic of trans-isomers. Lithium aluminum hydride reduces the dibromide to 2-butene, which by treatment with bromine is converted into meso-2,3-dibromobutane. The dipole moment of butadiene dibromide (1.63 D) was found to be closer to the dipole moment of trans-1,4-dibromo-2,3-dimethyl-2-butene (1.72 D) than to the dipole moment of the cis-isomers of the latter (2.49 D).

Bromination of 2,3-dimethyl-1,3-butadiene gives a mixture of two products, one of which is a liquid and the other crystalline. The first of these is unstable and partly changes into the crystalline form even after standing for a short period. Close examination revealed that both are 1,4-dibromo-2,3-dimethyl-2-butene. The trans-configuration was assigned to the crystalline form and the cis- to the liquid. We have isolated both of the dibromides of 2,3-dimethyl-1,3-butadiene. The C=C bond frequency of the liquid isomer was 1650 ± 4 cm^{-1}, and that of the crystalline isomer 1650 ± 2 cm^{-1}. Consequently, it is impossible to distinguish spectrographically between the cis- and trans-forms of tetrasubstituted ethylene.

We give below the Raman spectra of the products that we studied.

1,4-Dibromo-2-butene. M.p. 53° (spectrum plotted in CCl_4 solution). We give the frequencies of the most intense lines after deducting the CCl_4 frequencies.

$\Delta\nu$: 171 (2), 442 (2), 593 (5), 628 (5), 1177 (5), 1206 (6), 1300 (1), 1655 (10).

1,4-Dibromo-2-pentene. B.p. 52.5° at 2 mm, d_4^{20} 1.7313, n_D^{20} 1.5466. Found %: Br 69.39. $C_5H_8Br_2$. Calculated %: Br 70.17.

$\Delta\nu$: 186 (6), 233 (1), 305 (5), 422 (3), 503 (2), 533 (3), 593 (4 b), 623 (4), 663 (10 b), 801 (4), 923 (2), 976 (1), 1010 (3), 1049 (2), 1110 (2), 1167 (2), 1201 (3), 1229 (3), 1314 (2), 1361 (2), 1388 (1), 1657 (10).

2,5-Dibromo-3-hexene. B.p. 66.5° at 2 mm, d_4^{20} 1.6216, n_D^{20} 1.5355. Found %: Br 66.15. $C_6H_{10}Br_2$. Calculated %: Br 66.11.

$\Delta\nu$: 305 (3), 593 (2 b), 623 (2), 668 (2), 845 (3), 899 (2), 938 (1), 1063 (3), 1154 (4), 1186 (5), 1210 (3), 1309 (2), 1659 (10).

1,4-Dibromo-2-methyl-2-butene. B.p. 70.5° at 2 mm d_4^{20} 1.7743. n_D^{20} 1.5620.

$\Delta\nu$: 223 (4), 330 (2), 386 (2), 437 (5), 448 (2), 583 (5 b), 618 (6 b), 648 (4), 777 (6), 850 (2), 909 (1), 1000 (2), 1063 (3), 1150 (5), 1206 (8), 1239 (6), 1328 (1), 1393 (1), 1435 (1), 1458 (1), 1655 (10).

1,4-Dibromo-2,3-dimethyl-2-butene. a) Crystalline form. M.p. 47° (spectrum taken in CCl_4 solution).

$\Delta\nu$: 295 (5), 402 (1), 518 (3), 563 (2), 618 (2), 643 (4), 688 (2), 723 (3), 855 (3), 1650 (8).

b) Liquid form. B.p. 75° at 4 mm, d_4^{20} 1.5504, n_D^{20} 1.4988.

$\Delta\nu$: 171 (3), 212 (2), 319 (2), 458 (5), 488 (7), 518 (9), 583 (4 b), 613 (5), 638 (10 b), 653 (4), 718 (5), 752 (4), 835 (1), 865 (1), 918 (3), 1000 (3 b), 1111 (3), 1177 (1), 1210 (10), 1285 (8), 1384 (1), 1449 (2), 1591 (1), 1650 (10).

Diethyl ether of 2-butene-1,4-diol [3]. B.p. 169-170°, d_4^{20} 0.8717, n_D^{20} 1.4246, MR_D 42.26, calculated, 41.96. Found %: C 66.78; H 11.30. $C_8H_{16}O_2$. Calculated %: C 66.63; H 11.18.

$\Delta\nu$: 850 (2), 870 (1), 1015 (1), 1101 (2), 1153 (1), 1290 (1), 1346 (1), 1398 (1), 1486 (3), 1677 (5).

2-Butene-1,4-diol diacetate [4]. B.p. 135-136° at 10 mm, d_4^{20} 1.0858, n_D^{20} 1.1062, MR_D 42.05, calculated 41.98. Found %: C 55.68; H 7.11. $C_8H_{12}O_4$. Calculated %: C 55.8; H 7.03.

$\Delta\nu$: 171 (2), 310 (1), 377 (1), 432 (1), 638 (4), 835 (3), 879 (1), 967 (2), 1030 (3), 1177 (2), 1229 (2), 1266 (1), 1290 (2), 1309 (1), 1356 (1), 1384 (1), 1435 (2), 1458 (2), 1677 (10), 1736 (5).

SUMMARY

A study of the Raman spectra of the dibromides of butadiene and its nearest homologs, as well as of the diethyl ether and diacetate of 2-butene-1,4-diol, showed that the addition of bromine to these conjugated dienes proceeds according to a common mechanism. The 1,4-dibromides formed possess a trans-configuration.

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THE PROCESS OF FORMATION OF POLYAMIDE RESINS

IV. THE STEPWISE CHARACTER OF THE PROCESS OF FORMATION OF POLYAMIDE RESINS AND OF THE PRODUCTS OF REACTION OF ϵ-CAPROLACTAM WITH ADIPIC ACID

A. S. Shpitalnyi, K. E. Perepelkin and E. A. Meos

Although at the present day, the formation of polyamides is believed to be a stepwise process [1], papers have been published which attribute a radical character instead of a stepwise character to the formation of polyamides if the starting material is ϵ-caprolactam [2].

We have presented some evidence for the stepwise character of the transformation of ϵ-caprolactam into polymer [3,4]. For example, the products of reaction of ϵ-caprolactam with some dicarboxylic acids or amines were isolated, also low-molecular polymers which were intermediate products of the transformation of ϵ-caprolactam into high-molecular polyamides. The previously described products of reaction were obtained with an equimolecular ratio of components. Since we assumed that the isolation of low-molecular products with a larger number of links than in the preceding investigation is further evidence of the stepwise character of the formation of polyamides from ϵ-caprolactam, we made an attempt to obtain products of interaction with a molar ratio of starting components – adipic acid and ϵ-caprolactam – of 1:2 and 1:4. In this case we expected to obtain the compounds:

$$HOOC-(CH_2)_5-NH-CO(CH_2)_4-CO-NH-(CH_2)_5-COOH; \qquad (I)$$

$$HO-(CO(CH_2)_5-NH)_2-CO-(CH_2)_4-CO-(NH-(CH_2)_5-CO)_2-OH. \qquad (II)$$

The composition of these compounds was established by analysis of their silver salts.

A comparison of the properties of the silver salts of the products of reaction of ϵ-caprolactam with adipic acid with those of salts of adipic and other dicarboxylic acids established that some of their properties differ; in particular they differ in their solubility in water.

Solubility in Water of Silver Salts of some Dicarboxylic Acids

Prep. no.	Salt	Temp. (in °)	Solubility (in g per 100 g water)	Literature reference
1	Silver oxalate	18	0.034	[5]
2	Silver succinate	18	0.0176	[6]
3	Silver adipate	14	0.0166	[7]
4	The same	100	0.049	[7]
5	Silver salt of product of reaction of adipic acid with ϵ-caprolactam in equimolar ratio	17	0.082	–
6	The same	100	0.46	–

Since the silver salt of the product of reaction of ϵ-caprolactam with adipic acid was found to have a fairly high solubility, washing of the salts was effected in succession with small portions of water, alcohol and ether.

The external appearance of the products changed in dependence on the length of their molecules. Products of interaction whose molecules consist of two or three links have a waxy appearance. Products with four links in the molecule resemble a hard resin and have a conchoidal fracture. Analysis of the silver salts of these products showed that the adipic acid enters completely into reaction with ϵ-caprolactam, since it was not detected in the reaction products.

When the adipic acid was replaced by benzoic acid, part of the latter did not enter into reaction even with a considerable excess of ϵ-caprolactam. This interesting observation was made by A. Matthes [2] and confirmed by our experiments. Matthes explained this phenomenon by the susceptibility of the benzoic acid – ϵ-caprolactam reaction product to decomposition during the reaction with formation of radicals of ϵ-caprolactam.

If this interpretation were correct, then the phenomenon should also be observed in the reaction of adipic acid with ε-caprolactam, but this is not the case.

Considering that the boiling point of adipic acid is 265° (at 100 mm) [8], whereas benzoic acid can sublime at as low as 100° [9], and that the reaction temperature is 240°, there can be no doubt at all that in the reaction of benzoic acid with ε-caprolactam, a part of the benzoic acid will be outside the sphere of reaction. This must be the actual reason why benzoic acid is found in the cooled reaction mass even with an excess of the ε-caprolactam reacting with it.

Consequently, the experimental material of the present investigation, likewise confirms the stepwise character of the transformation of ε-caprolactam into polyamide.

EXPERIMENTAL

Reaction of ε-Caprolactam with Adipic Acid in Equimolecular Ratio and Properties of the Final Product

The product of interaction of adipic acid with ε-caprolactam in equimolecular ratio was prepared as previously described [3]. It forms a grey melt with a waxy appearance and consistency, soluble in water on heating, slightly soluble in alcohol, insoluble in ether and benzene.

The silver salt of the product is prepared in the following manner. The melt is dissolved in water with heating and treated with excess of calcium carbonate until carbon dioxide ceases to come off. The solution is filtered and to the filtrate is added an excess of 5-8% solution of silver nitrate. The white flocculent precipitate is collected, washed with a little water and then with alcohol (until it gives a negative test for calcium with alcoholic oxalic acid) and dried after washing with ether. Analysis was carried out by the usual procedure [10].

0.2795 g sub.: 0.1690 g AgCl. 0.2800 g sub.: 0.1703 g AgCl. Found %: Ag 45.53, 45.77. $C_{12}H_{19}O_5NAg_2$. Calculated %: Ag 45.61.

The solubility of the silver salt of the product of reaction in 100 g water at 17° is 0.082 g; at 100°, it is 0.46 g.

Reaction of ε-Caprolactam with Adipic Acid in 2:1 Molar Ratio and the Properties of the Product

The product of interaction and its silver salt were prepared by the above procedure. The outward appearance of the melt and its properties were the same as those of the product of equimolar amounts of the components.

Reaction of ε-Caprolactam with Adipic Acid in 4:1 Molar Ratio and the Properties of the Product

0.7307 g adipic acid and 2.2632 g ε-caprolactam in a sealed tube (from which the air had been purged with carbon dioxide) were heated at 240° for 25 hours. The white melt was a hard resin (conchoidal fracture), poorly soluble in water even when boiled, insoluble in alcohol, ether and benzene.

The silver salt of the reaction product was prepared and analyzed as before (when dissolved by addition of nitric acid, the dicarboxylic acid – the product of reaction of ε-caprolactam with adipic acid – does not dissolve and must be filtered off).

0.2532 g sub.: 0.0888 g AgCl. 0.2662 g sub.: 0.0950 g AgCl. Found %: Ag 26.39, 26.86. $C_{30}H_{52}O_8N_4Ag_2$. Calculated %: Ag 26.56.

The reaction product, therefore, has formula (II).

Reaction of ε-Caprolactam with Benzoic Acid in 1:1 Molar Ratio

2.442 g benzoic acid and 2.2632 g ε-caprolactam (equimolar ratio) were heated in an ampoule, from which the air had previously been displaced by carbon dioxide, for 46 hours at 240°. Part of the unreacted benzoic acid adhered to the walls of the ampoule. The product had a soft, waxy consistency.

0.3118 g sub.: 0.1033 g AgCl. 0.3100 g sub.: 0.1030 g AgCl. Found %: Ag 24.93, 25.01. Calculated %: Ag for products of interaction of ε-caprolactam with benzoic acid (in 1:1 molar ratio) 33.48; (in molar ratio of 2:1) 24.78.

Consequently, only a portion of the benzoic acid had reacted with caprolactam. In order to establish whether the reaction mass contains benzoic acid, 1.9170 g of the latter was extracted with ether. Weight of extract was 0.9794 g (51.2%). It had a waxy consistency. The residue after extraction (0.9334 g or 48.7%) formed hard pellets.

The product obtained after evaporation of the ethereal extract was titrated with 0.1 N NaOH solution in presence of phenolphthalein.

0.0693 g sub.: 3.95 ml 0.1 N NaOH. 0.0700 g sub.: 3.96 ml 0.1 N NaOH.

Calculated on benzoic acid the ethereal extract contains 70.5, 70.0%, while calculated on benzoylaminocaproic acid it contains 135.8, 135.0%. Consequently, the portion extracted consists of benzoic acid (34.2%) and benzoylaminocaproic acid (65.8%). ϵ-Caprolactam is absent from the portion extracted because it is capable of being completely converted to calcium salt (after treatment of the aqueous solution of the extracted portion with calcium carbonate, filtration and drying, a product is obtained which is completely insoluble in ether).

Reaction of ϵ-Caprolactam with Benzoic Acid in 2:1 Molar Ratio

The product of reaction of ϵ-caprolactam with benzoic acid in 2:1 molar ratio and its silver salt were prepared as in the preceding case. The silver salt is a white powder.

0.1455 g sub.: 0.0446 g AgCl. 0.1500 g sub.: 0.0453 g AgCl. Found %: Ag 23.07, 22.73. Calculated %: Ag for products of reaction of ϵ-caprolactam with benzoic acid (in 2:1 molar ratio) 24.78; (in 3:1 molar ratio) 19.66.

It follows from the analytical data that in this case also, not all the benzoic acid had entered into reaction with the caprolactam.

SUMMARY

1. Isolation of the products of interaction of adipic acid with ϵ-caprolactam in 1:2 and 1:4 molar ratios yielded supplementary evidence for the stepwise-polymerization process during the formation of a polyamide from ϵ-caprolactam.

2. A description is given of some of the properties of the products of reaction of adipic acid with ϵ-caprolactam in various molar ratios; determinations were made of the solubility of the silver salt of the product of reaction of equimolar amounts of the starting components.

3. It was shown that the presence of benzoic acid in the reaction mixture after interaction of the former with excess of ϵ-caprolactam is due to the low temperature of sublimation of benzoic acid.

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* See Consultants Bureau Translation, page 1311.

** See Consultants Bureau Translation, page 1447.

ACYLATION OF THE ENOL FORM OF ACETALDEHYDE

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A number of transformations of acetaldehyde can proceed with participation of vinyl alcohol as the reactive form of acetaldehyde. An example of such a transformation is evidently the reaction of acetaldehyde with acetic anhydride [1-3] $CH_3-CHO \rightarrow CH_3CH(OCOCH_3)_2 \rightarrow CH_2=CH-OCOCH_3$.

The reaction between acetaldehyde and acetic anhydride, leading to formation of ethylidene diacetate, has found practical application in the production of vinyl acetate [4]. For this purpose ethylidene diacetate is subjected to thermal decomposition. It is found that in this reaction, the acetaldehyde can be successfully replaced by paraldehyde.

Reactions of the same class are the formation of ethylidene diacetate by heating acetyl chloride with acetaldehyde [5], the formation of phenylvinyl acetate [6] and α-chloro- and α-bromovinyl acetates [7] from the respective aldehydes and acetic anhydride.

Acetaldehyde has been observed to form a compound $(H_2C=CHO)_2Hg \cdot HgO$ [8] and mercuric chloride in aqueous potassium carbonate solution; the yield of this mercury compound was found to be directly proportional to the concentration of alkali in the solution [9].

Nesmeyanov and Lutsenko [10] obtained chloromercuriacetaldehyde when starting from vinyl ethers. Treatment of this compound with acetyl chloride or benzoyl chloride in xylene readily leads to vinyl benzoate:

$$ClHgCH_2CHO + RCOCl \rightarrow CH_2=CH-O-COR + HgCl_2.$$

Enol acetates of acetaldehyde, phenylacetaldehyde, isobutyraldehyde and enanthal [11] have also been obtained by heating these aldehydes with acetic anhydride in presence of potassium acetate.

Acetylation of acetaldehyde, paraldehyde, butyraldehyde and isobutyraldehyde with isopropenyl acetate [12] also yielded the enol acetates. The yield of vinyl acetate here was 78% when starting from acetaldehyde and 88% of the theoretical when starting from paraldehyde.

Some catalytic processes with acetaldehyde as catalyst, for example the hydration of dicyanogen to oxamide [13], pass through the stage of formation of vinyl alcohol.

Methods are described in the literature for preparation of a series of perfectly stable α-substituted vinyl alcohols not susceptible to transition to the keto form [14], for example 2-mesityl-2-phenylvinyl, 2-duryl-2-phenyl-, 2-(3-bromomesityl)-2-phenyl- and 2,2-(2,4,6-triisopropylphenyl)-vinyl alcohols.

X-ray crystallographic investigations showed that the stability of these vinyl alcohols is due to the spatial arrangement of the groups which hinder rearrangement to the keto form.

On the basis of an analysis of the above-cited literature data we concluded that it was entirely probable that any desired vinyl esters could be obtained from acetaldehyde in presence of enolizing substances.

The reaction was performed in a medium of organic tertiary bases (pyridine, quinoline and dimethylaniline) with acetaldehyde and certain other aldehydes. Anhydrides and acid chlorides were tried out as enolizing media. Similar experiments were also run with paraldehyde.

The principal constants of the prepared vinyl esters were determined; in some cases also the iodine numbers and the saponification numbers. Esters containing a large number of double bonds were analyzed by ozonization.

Acylation of acetaldehyde with anhydrides gives low yields of vinyl esters. When using anhydrides of higher acids, the formation of vinyl esters was not generally observed. Acylation of the enol form of acetaldehyde with acid chlorides in all cases led to vinyl esters in high yields.

The best results were had when pyridine was the reaction medium. Quinoline reacts very violently with the acid chlorides and in some cases causes resinification of the acetaldehyde. Dimethylaniline has no advantage over pyridine and in some cases hinders the separation of the vinyl esters in the pure state.

EXPERIMENTAL

The first series of experiments was performed with acetaldehyde and various anhydrides. The anhydride was gradually added to a mixture of acetaldehyde and anhydrous quinoline, pyridine or dimethylaniline with continuous stirring and cooling with iced water; after the whole of the anhydride had been added, the mixture was heated to 60-80° under reflux with iced water cooling. The reaction products were then poured into water, separated in a separating funnel and repeatedly washed by shaking with water. After drying over anhydrous sodium sulfate, the product was fractionated (if necessary in vacuum).

The results of this part of the investigation are set forth in Table 1.

TABLE 1

Acylation with Anhydrides

Anhydride	Medium	Yield of ester (in % of theoretical)	
		with acetaldehyde	with paraldehyde
Acetic	Quinoline	36	20
	Dimethylaniline	24	–
	Pyridine	20	–
Propionic	Quinoline	29	22
	Dimethylaniline	27	–
	Pyridine	16.5	–
Butyric	Quinoline	25	16
	Dimethylaniline	32	–
	Pyridine	14	–
Stearic	Quinoline	0	–

All the experiments listed in the table were carried out with molar ratios of anhydride to acetaldehyde and to the amines of 1:0.5:3. A few experiments showed that these ratios are the optimum for maximum yields of esters.

Stearic anhydride did not react either in the above conditions or in any of their variations. In no case was the formation of ethylidene glycol esters observed.

A second series of experiments was performed with acetaldehyde, paraldehyde and acid chlorides in a medium of dimethylaniline, pyridine and quinoline.

To a mixture of acetaldehyde or paraldehyde with quinoline, dimethylaniline or pyridine, cooled with iced water or snow-salt mixture, was gradually added the acid chloride with stirring. The reaction mixture was afterwards slowly heated to 50-60° and then poured into water or onto ice; the ester layer was separated, dried over anhydrous sodium sulfate and fractionated (sometimes in vacuum).

Molar ratios: 2 moles acetaldehyde were reacted with 1 mole chloride of a mono-basic acid or 0.5 mole chloride of a dibasic acid in presence of 3-5 moles of base.

Results are set forth in Table 2.

TABLE 2

Acylation with Chloroanhydrides

Acid chloride	Medium	Yield of ester (in % of theoretical)	
		with acetaldehyde	with paraldehyde
Acetyl chloride	Quinoline	40.5	28.0
Stearyl chloride	Quinoline	92.0	65.0
Acetyl chloride	Dimethylaniline	89.0	–
Stearyl chloride	Dimethylaniline	62.0	–
Acetyl chloride	Pyridine	86.0	85.0
Stearyl chloride	Pyridine	88.0	68.0

The results obtained justify the conclusion that our method is applicable to the synthesis of vinyl esters. We carried out the reaction with 29 subatances and obtained in all cases the corresponding vinyl esters.

Table 3 contains the constants and yields of esters prepared by this method. The yields of vinyl esters enumerated in the table were obtained when using pyridine as the reaction medium (with acetaldehyde). When using quinoline, the yields of esters of higher fatty acids were slightly increased but those of esters of lower aliphatic acids were considerably reduced. Replacement of acetaldehyde by paraldehyde in all cases lowered the yield of vinyl esters.

TABLE 3

Acylation with Acid Chlorides

Acid chloride	Yield of ester (in % of theor.)	B.p. (in °) (pressure in mm)		d_4^{20}		n_D^{20}	
		found	literature data	found	literature data	found	literature data
Acetyl	82	72-73 (760)	73 (760) [15]	0.9321	0.9342 [15]	1.3958	1.3958 [15]
Valeryl	78	134 (760)	133-134 (760) [16]	0.9080	–	1.4170	–
Caproyl	77	162 (760)	165-170 (760) [16]	0.8832	0.8837 (30°) [17]	1.4160	1.4152 (30°) [17]
Enanthyl	79	182-183 (760)	–	0.8992	–	1.4206	–
Capryl	78	90 (10)	94 (13) [16]	0.8889	0.889 [18]	1.4260	1.4271 [18]
Pelargonyl	82	130 (42)	133-133.5 (50) [17]	0.8690	0.8689 (30°) [17]	1.4289	1.4291 (30°) [17]
Caprinyl	80	119-120 (10)	148 (50) [17]	0.8681	0.8670 (30°) [17]	1.4329	1.4320 (30°) [17]
Undecyl	82	124-125 (8)	125 (10) [19]	0.8820	–	1.4355	–
Lauryl	86	123-124 (4)	123 (4) [16]	0.8641	0.8770 [18]	1.4371	1.4386 [18]
Myristyl	88	152 (3)	150 (3) [16]	0.8620	0.8617 (30°) [17]	1.4412	1.4407 (30°) [17]
Palmityl	79	162 (2)	165 (2) [16]	0.8612	0.8602 (30°) [17]	1.4441	1.4438 (30°) [17]
Stearyl	88	166-167 (2)	167 (2) [16]	0.8521 (30°)	0.8517 (30°) [17]	1.4426 (30°)	1.4423 (30°) [17]
Trimethylacetyl	86	113-114 (760)	110-112 (760) [18]	0.8820	0.873 [18]	1.4072	1.4068 [18]
Phenylacetyl	80	126-128 (32)	88-90 (4) [16]	1.0271	–	1.5002	–
α-Chlorobutyryl	82	157-158 (760)	–	1.0610	–	–	–
β- Chlorobutyryl	80	163-164 (760)	–	1.0581	–	1.4260	–
γ-Chlorobutyryl	80	179-180 (760)	–	1.0702	–	1.4486	–
Bromoacetyl	51	76 (40)	–	1.5058	–	1.5556	–
Iodoacetyl	34	72-73 (20)	–	1.8101	–	1.4844	–
Methacryl	75	111-112 (760)	–	1.4029	–	–	–
Undecenyl	75	127 (10)	–	0.8780	–	1.4462 (25°)	–
Oleyl	68	172-173 (2)	173 (2) [16]	0.8699	0.869 [18]	1.4538	1.4533 [18]
Adipyl	54	125-126 (12)	110-124 (10) [19]	–	–	–	–
Sebacyl	62	142 (3)	–	–	–	–	–
Fumaryl	38	138 (1)	–	–	–	–	–
Maleyl	35	94 (10)	–	–	–	–	–
Benzoyl	89	75 (4)	72-74 (3) [16]	–	1.0706 [18]	–	1.5259 [18]
o-Phthalyl	66	138-139 (5)	–	–	–	–	–
β-Naphthoyl	68	142-143 (2)	153 (4) [16]	–	–	–	–

A small amount (up to 1%) copper resinate was added to the vinyl esters prior to distillation to inhibit polymerization.

Reactions between butyraldehyde and enanthal and acetyl chloride in a pyridine medium were performed in exactly the same manner. The enol acetate of butyraldehyde was obtained in a yield of 78.5% of the theoretical and had b.p. 129-130°; the enolacetate of enanthal was obtained in 52% yield and had b.p. 88-89° at 17 mm.

It should be pointed out that the pyridine, quinoline, dimethylaniline and acetaldehyde used in the reactions must be thoroughly dried, since even traces of moisture in the starting materials considerably reduce the yield of vinyl ester. Freshly distilled reagents are also desirable.

SUMMARY

1. The results of our present investigation confirm that acetaldehyde reacts in its tautomeric form (vinyl alcohol) in presence of enolizing substances.

2. For the first time, the vinyl esters of the following acids were prepared: enanthic, undecyl, α-, β-, and γ-chlorobutyric, bromoacetic, iodoacetic, methacrylic, undecylenic, sebacic, fumaric, maleic and o-phthalic.

3. The method was extended to the preparation of enol acetates of other aldehydes.

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THE ROLE OF THE OXIDATION-REDUCTION PROPERTIES OF α-HYDROXY KETONES IN INITIATED POLYMERIZATION*

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Intermolecular and intramolecular oxidation-reduction reactions [1], previously designated as simultaneous oxidation-reduction reactions [2], are characterized by migration of oxygen within a molecule without change of composition or between different molecules, for example, in the removal or addition of oxygen-containing molecules (water, alcohol, etc.), as was discussed in previous papers [1, 3].

Hydroxyaldehydes and hydroxyketones, for which intramolecular oxidation-reduction, hydroxyketonic and acidic transformations are known, are characterized by great ease of oxidation of alcoholic groups (formation of aldehydoketones and diketones), and also by reduction of their carbonyl groups to alcohol groups with transformation into glycols. Danilov and Venus-Danilova [4] have studied the oxidation of a ketone-alcohol to a diketone and reduction of the latter to ketoalcohol.

For the understanding of the hydroxyketonic and acidic transformation of α-hydroxyaldehydes and α-hydroxyketones, great interest attaches to the characterization of hydroxycarbonyl compounds in respect of the oxidizability of their alcohol group and of the reducibility of the carbonyl group with reference to ease of cleavage of hydrogen atoms from the alcohol groups and capture of the detached hydrogen atoms by the carbonyl groups. The susceptibility to reduction of carbonyl groups can be evaluated from polarographic data [5].

At the present time extensive use is made at home and abroad of oxidation-reduction systems in the initiation of polymerization of unsaturated compounds. The action of a peroxide (initiator) in polymerization is intensified by introducing into the medium a substance which is readily oxidized and reduced, for example, benzoin and other hydroxycarbonyl compounds (in Kern's experiments [6]) and a polyvalent metal ion, for example, iron salts of organic acids which influence the decomposition of peroxide.

With the objective of evaluating the oxidation-reduction properties of ketoalcohols with primary and secondary alcohol groups and in dependence on the radicals, we studied the kinetics of polymerization of styrene in an oxidation-reduction system with participation of two isomeric ketoalcohols – propionylcarbinol and methylacetylcarbinol; benzoin was used for comparison. The great activity of 1,3-dihydroxy-2-propanone benzoin reducing substance was confirmed by I. Kolthoff in the copolymerization of butadiene and styrene [7]. The extent of polymerization is conveniently measured by the dilatometric method as applied by B.A. Dogadkin and co-workers [8].

Our experiments on the polymerization of styrene in presence of an oxidation-reduction system (benzoyl peroxide, iron naphthenate, ketoalcohol) led to the conclusion that of the three alcohols compared, the greatest activity is manifested by benzoin. The isomeric α-hydroxybutanones (methylacetylcarbinol and propionylcarbinol) were inferior to benzoin; they showed, however, considerable activity, although the primary ketoalcohol was less active than the secondary isomer (methylacetylcarbinol). It should be mentioned that polarographic experiments [5] revealed a lower susceptibility to reduction on the part of propionylcarbinol in comparison with methylacetylcarbinol, and the latter in turn had a lower susceptibility to reduction than benzoin. It might be thought that the susceptibility to oxidation to dicarbonyl compounds of these ketoalcohols also rises from propionylcarbinol to methylacetylcarbinol to benzoin, but this point is still under investigation. A good criterion of the oxidation-reduction properties of ketoalcohols must be their influence (in dependence on the structure) on the rate of polymerization when they are used in oxidation-reduction systems.

On the basis of the results obtained, we may conclude that the ketoalcohols under consideration may be arranged in the following order in respect of their activity in oxidation-reduction systems during polymerization:

benzoin > methylacetylcarbinol > propionylcarbinol.

Ketoalcohols which function as reducers in oxidation-reduction systems during polymerization are oxidized. Consequently the relative susceptibility to oxidation of the above ketoalcohols corresponds to a series in which they are arranged in order of reductive ability as determined by polarographic measurements as previously described [5].

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* This is the third communication in a series on "Hydrolytic and solvolytic intermolecular and intramolecular oxidation-reduction"; see Danilov, J. Gen. Chem., 18,200 (1948).

This concurrence in susceptibility to oxidation and reduction is probably not a general rule for all ketoalcohols, but it results in the case of our ketoalcohols in benzoin having increased susceptibility both to oxidation and reduction due to the presence in it of phenyl groups.

The comparison in this respect of propionylcarbinol and methylacetylcarbinol indicates that a primary alcoholic group weakens the oxidation-reduction properties of a molecule. Evidently the $COCH_2OH$ group is less susceptible to oxidation and reduction than the COCHOH group. These properties of ketoalcohols must evidently be correlated with the facts which indicate that α-hydroxybutyraldehyde isomerizes to methylacetylcarbinol whereas in the same conditions the isomerization of propionylcarbinol to methylacetylcarbinol is not observed.

EXPERIMENTAL

Experiments on polymerization of styrene were carried out at 50° in a block, using as the initiating system (as previously used by Kern [6]): benzoyl peroxide, iron (Fe^{+++}) naphthenate and ketoalcohol. A comparison was made between benzoin, methylacetylcarbinol (acetoin) and propionylcarbinol (1.25 %). An experiment was run in parallel without addition of ketoalcohol. The extent of polymerization was determined (as mentioned above) by the dilatometric method —contraction of volume of the system on transition from monomer to polymer.*

The starting substances were carefully purified. Before an experiment, the styrene which had been purified in the usual manner and dried, was distilled in vacuum in a current of nitrogen; b.p. 40° at 14 mm.

Benzoyl peroxide was recrystallized from chloroform with addition of methanol at room temperature; m.p. 104°.

The ketoalcohols were prepared and purified by the previously described methods [9, 10]. The following were used: Propionylcarbinol with b.p. 64° at 24 mm, n_D^{20} 1.4242 methylacetylcarbinol with b.p. 56° at 34 mm, n_D^{20} 1.4200; benzoin with m.p. 133°.

In a flask with three taps (Schmidlin-Schlenk type), ensuring complete exclusion of [11] from the liquid, was prepared a solution of styrene with addition of 1.25% benzoyl peroxide and 0.05% iron naphthenate. Quantities were 158 ml (142.2 g) styrene, 1.78 g benzoyl peroxide and 0.7 g iron naphthenate. The glass ampoules used had a graduated scale for measurement of contraction, two necks and a pouch for addition of the ketoalcohol. The volume of each ampoule was measured in advance upto a specified graduation mark. The ampoules were connected to a set of taps linked in turn to a vacuum pump and a nitrogen supply. The system was pumped out three times and purged with nitrogen between each pumping. The ampoules were filled, in countercurrent with nitrogen, with the prepared solution from the Schlenk apparatus, in each case up to a specific mark on the graduation. Into the pouches of the ampoule were also charged the calculated weights of ketoalcohols. One ampoule (control) was left without this addition. After the ampoules had been filled, their necks were sealed off while a stream of nitrogen was passed. Before immersion in the ultrathermostat, each ampoule was well shaken to enable the ketoalcohol to fall into the styrene solution. After keeping in the thermostat for 15 minutes, the level of the liquid in each ampoule was noted. Measurements were made every hour over a period of 20 hours. Curves of styrene polymerization velocity as a function of the ketoalcohol additions are plotted in the diagram, the abscissas of which are durations and the ordinates are % of polymerized styrene calculated from the formula [12]:

$$S = \frac{\Delta\nu_{obs.}}{\Delta\nu_{max}} \cdot 100$$

where S = percentage polymerization;

$\Delta\nu_{obs.}$ = observed contraction of volume (in ml);

$\Delta\nu_{max}$ is calculated for each ampoule from the formula for styrene:

$$\Delta\nu_{max} = 16.6 \cdot \nu \text{ of ampoule.}$$

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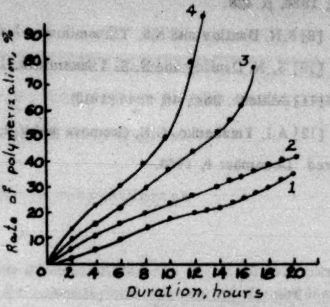
[*] We express our thanks for advice to the senior scientific assistant of the Institute of High-Molecular Compounds of the Academy of Sciences of the USSR, E.I. Tinyakova.

We see from the diagram that after 10 hours' heating the polymerization in the ampoule without addition of ketoalcohol had proceeded to the extent of 18%; with addition of propionylcarbinol it was 23%; with addition of methylacetylcarbinol it was 36%; and with addition of benzoin it was 50%. The most active of the three ketoalcohols was benzoin — a ketoalcohol containing phenyl radicals. Of the other two isomeric ketoalcohols, the first was less active than the second, although the addition of propionylcarbinol slightly accelerated polymerization in comparison with the control.

Further observations of the course of polymerization, with assumption of the suitability of the above formula, gave the following information: In the case of benzoin, after heating for 10 hours the rate of polymerization of styrene increased sharply; after 13 hours' heating the extent of polymerization, calculated from the above formula, reached nearly 100%. In the ampoule with addition of methylacetylcarbinol, after 14 hours heating the polymerization rate sharply increased and attained a 50% value, rising again after 17 hours to 73.5%. After 20 hours heating at 50° in the experiments without addition of ketoalcohol, polymerization proceeded to the extent of 36%, while with addition of propionylcarbinol it was 42%.



Curves of styrene polymerization velocities in presence of benzoyl peroxide (1.25%), iron naphthenate (0.05%) and ketoalcohol (1.25%). 1) Without addition of ketoalcohol; 2) with addition of propionylcarbinol; 3) with addition of methylacetylcarbinol; 4) with addition of benzoin.

Further observations were made at room temperature and revealed that in the experiments without addition of ketoalcohol the polymerization did not proceed any further; in those with addition of propionylcarbinol there was a slow decrease of volume which after 50 hours observation (after previously keeping for 20 hours at 50°) corresponded to 67% polymerization of the styrene. In the control experiment the polymerization after this period had proceeded to the extent of 38%.

SUMMARY

1. Participation of hydroxycarbonyl compounds in oxidation-reduction systems during polymerization of unsaturated compounds can serve as a measure of the oxidation-reduction properties.

2. Experiments on styrene polymerization were carried out with the help of an oxidation-reduction system consisting of 1.25% benzoyl peroxide, 0.05% iron (Fe^{+++}) naphthenate and 1.25% ketoalcohol (propionylcarbinol, methylacetylcarbinol, or benzoin).

The experiments showed that benzoin was the most active agent in styrene polymerization, followed in order by methylacetylcarbinol and propionylcarbinol.

3. The susceptibility to oxidation of the ketoalcohols, manifested in their participation in the oxidation-reduction system during styrene polymerization, is in harmony with data from experiments on determination of their susceptibility to reduction at the dropping mercury cathode.

4. The oxidation-reduction properties of propionylcarbinol and methylacetylcarbinol are consistent with the fact that propionylcarbinol does not isomerize to methylacetylcarbinol in the conditions in which the latter is formed from α-hydroxybutyraldehyde.

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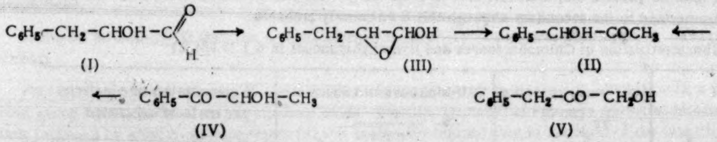
ISOMERIZATION OF *a* -HYDROXYALDEHYDES

XIII. TRANSFORMATIONS OF *a* -HALOGENO - AND *a* -HYDROXYKETONES WITH A PRIMARY ALCOHOLIC GROUP

S.N. Danilov and N.S. Tikhomirova-Sidorova

In papers by S.N. Danilov and E.D. Venus-Danilova it was shown by reference to a series of examples [1] that *a* -halogeno- and *a* -hydroxyaldehydes of the aliphatic and polymethylene series are transformed into *a* -hydroxyketones and isomeric acids (in analogy with the epimeric and saccharinic rearrangement of monoses) in conditions of acidic and alkaline-salt catalysis [2]. These rearrangements can be predicted (S.N. Danilov [1]) on the basis of isomeric transformations in the group of monoses [3] and dihalogenoketones [4], as well as according to A.E. Favorsky's alcoholic-oxide scheme proposed for interpretation of the acidic transformation of monohalogenoketones [5] and later (1928) for explanation of the isomerization of ketoalcohols [6].

Benzylglycolaldehyde (I) is isomerized [7] to a secondary ketoalcohol – phenylacetylcarbinol (II). The other isomeric ketoalcohol – methylbenzoylcarbinol (IV), was not isolated. It was known [6, 8] that methylbenzoylcarbinol isomerizes to phenylacetylcarbinol. More noteworthy, however, is the fact that benzylglycolaldehyde does not yield a ketoalcohol with a primary alcoholic group (V) which might have been formed in accordance with Favorsky's alcoholic-oxide scheme (III) and as the closest isomer of the hydroxyaldehyde:



$$C_6H_5-CH_2-CHOH-C\overset{O}{\underset{H}{\diagdown}} \longrightarrow C_6H_5-CH_2-\underbrace{CH-CHOH}_{O} \longrightarrow C_6H_5-CHOH-COCH_3 \longleftarrow$$

(I) (III) (II)

$$\longleftarrow C_6H_5-CO-CHOH-CH_3 \qquad C_6H_5-CH_2-CO-CH_2OH$$

(IV) (V)

The transformation of *a* -hydroxybutyraldehyde [9] also leads directly to 3-hydroxy-2-butanone which contains a secondary alcoholic group.

Similarly *a* -hydroxyenanthaldehyde forms a hydroxyketone with an acetyl group on rearrangement [10]. It was first suggested [7] that the ketoalcohol with a primary alcohol group is an intermediate product in the isomerization of *a* -hydroxyaldehydes (monosubstituted glycolaldehydes) to *a* -hydroxyketones and is transformed in the instant of formation into a ketoalcohol with a secondary alcohol group.

A few years ago the problem was posed [11] of synthesis of ketoalcohols containing a primary alcoholic group for the study of their possible role in the intermediate stage of isomerization of *a* -hydroxyaldehydes to ketoalcohols. In our previous paper [12] we described monochloroketones corresponding to methylethyl ketone, and we showed that 1-chloro-2-butanol may form, on hydrolysis of the chlorine, two isomeric ketoalcohols, i.e., rearrangement takes place to give an isomeric ketoalcohol with a secondary alcohol group. We have now supplemented the data in this field with the aim of establishing whether primary *a* -ketoalcohols are transformed into secondary in conditions similar to those of the hydroxyketonic rearrangement of *a* -hydroxyaldehydes. The possibility of isomerization of halogenoketones and their corresponding ketoalcohols with a primary alcohol group into saturated acids was also investigated.

An investigation was made of primary ketoalcohols 1-hydroxy-2-butanone $CH_3CH_2COCH_2OH$ and phenylacetol (V), the heating of which in presence of sulfuric acid was expected to lead to ketoalcohols with secondary alcoholic groups due to isomerization of *a*-hydroxybutyraldehyde and benzylglycolaldehyde. However, neither 3-hydroxy-2-butanone nor phenylacetylcarbinol was obtained in our conditions from ketoalcohols with a primary alcohol group. Evidently the transformation of *a*-hydroxyaldehydes into secondary *a*-ketoalcohols does not proceed through the stage of a primary ketoalcohol.

In our experiments two ketoalcohols – 1-hydroxy-2-butanone and the isomeric 3-hydroxy-2-butanone (VIII), were obtained from chloromethylethyl ketone (1-chloro-2-butanone) (VI) and 1-hydroxy-2-butanone (VII) respectively, as reported previously [12], on heating in an alkaline or aqueous medium with salts of lead or silver:

$$\underset{(VI)}{CH_3-CH_2-CO-CH_2Cl} \xrightarrow[PbO, KOH]{100^\circ} \underset{(VII)}{CH_3-CH_2-CO-CH_2OH} + \underset{(VIII)}{CH_3-CHOH-CO-CH_3}$$

The presence of the secondary ketoalcohol (VIII) was proved by isolation of its dimer (2, 3-butanedione) on oxidation, and by the preparation of its semicarbazone, phenylosazone, p-nitrophenylhydrazone and 2,4-dinitrophenylhydrazone.

The yield of 3-hydroxy-2-butanone is increased by choosing more drastic conditions of hydrolysis of 1-chloro-2-butanone. This indicates the possibility of isomerization of 1-hydroxy-2-butanone into 3-hydroxy-2-butanone, but suitable conditions of isomerization were not found. If such a transformation is indeed possible, then it evidently takes place in special conditions.

When using 7% alkali and lead hydroxide, however, heating to 150° causes the hydroxyketonic transformation of the chloroketone to proceed wholly with formation only of 3-hydroxy-2-butanone. In these conditions, on the other hand, 1-hydroxy-2-butanone does not isomerize to the secondary ketoalcohol. Consequently we can assume that the isomeric transformation is completed in the instant of action of the reagent on the chloroketone. Assuming that the chloroketone is enolized in the alkaline medium, the transformation may be represented as follows (via the allylic rearrangement):

$$CH_3-CH_2-CO-CH_2Cl \longrightarrow \underset{(IX)}{CH_3-CH=COH-CH_2Cl} \longrightarrow \underset{(X)}{CH_3-CHCl-COH=CH_2} \longrightarrow CH_3-CHOH-CO-CH_3.$$

Allylic rearrangement takes place in the enolic form of 1-chloro-2-butanol (IX) with formation of the enolic form of 3-chloro-2-butanone (X). Subsequently, due to hydrolysis, the chlorine is replaced by hydroxyl, and 3-hydroxy-2-butanone is formed.

It is evident that in the case of 1-hydroxy-2-butanone itself the allylic rearrangement with translocation of hydroxyl to the β-position does not take place since this ketoalcohol could not be isomerized to 3-hydroxy-2-butanone. It must be pointed out, however, that no proof has yet been forthcoming that the primary chloroketone can be isomerized to the secondary although this is extremely probable.

Polarographic Characterization of Chlorobutanones and Hydroxybutanones in 0.1 N NH_4Cl

Substance	Half-wave potential $E_{1/2}$ (in V)	Diffusion current constant $\frac{i_d}{c}$ (in $\frac{\mu A}{mole}$)	Consumption of electrons per mole of substance
1-Chloro-2-butanone	− 1.066	3560	0.513
3-Chloro-2-butanone	− 1.077	2248	0.353
1-Hydroxy-2-butanone	− 1.790	1610	0.290
3-Hydroxy-2-butanone	− 1.750	8960	0.470

Intramolecular oxidation-reduction transformations in chloroketones and ketoalcohols, when isomerization is accompanied by reduction of some carbon atoms and by oxidation of others, must be intimately bound up with the susceptibility to reduction of the isomerizing substances. For the comparison of ketoalcohols and chloroketones in respect of reduction we made use of the polarographic method. The results of the polarographic experiments were described in detail in an earlier paper by Bobrova and Tikhomirova-Sidorova [13] from which we quote some data in slightly modified and shortened form. We see from the table above that the primary chloroketone and 1-hydroxy-2-butanone, judging by all their electrochemical characteristics ($\frac{i_d}{c}$, α), are reduced with greater facility than the corresponding secondary compounds. This is in harmony with the fact that in the chloroketones $CH_3CH_2COCH_2Cl$ and $CH_3CHClCOCH_3$ the chlorine of the methyl group, due to its negative inductive effect, will more strongly repel the electrons of the carbonyl carbon than the atoms of chlorine of the ethyl group whose negative inductive effect overlaps with the positive inductive effect of the methyl group. Consequently, on the basis of these considerations, the primary chloroketone must be reduced more readily than the secondary isomer, as we found experimentally.

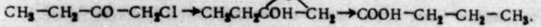
The polarographic behavior of the primary ketoalcohol is the opposite, in the given conditions, to that of the corresponding primary chloroketone in comparison with the secondary chloroketone.

In the light of the data obtained, the reduction of 3-hydroxy-2-butanone proceeds with greater facility than the reduction of 1-hydroxy-2-butanone; consequently greater difficulty must attend the intramolecular oxidation-reduction of the primary ketoalcohol, which is expected to result in reduction of the carbonyl group and formation of the secondary ketoalcohol. The carbonyl group of the latter ketoalcohol possesses a greater susceptibility to reduction than that in the ketoalcohol with a primary alcohol group. According to the polarographic data, the transformation of 1-hydroxy-2-butanone into 3-hydroxy-2-butanone is hindered, in accord with our unsuccessful attempts to isomerize 1-hydroxy-2-butanone.

This again confirms that the transformation of α -hydroxybutyraldehyde into 3-hydroxy-2-butanone via 1-hydroxy-2-butanone is highly improbable.

The observation of the greater facility of reduction of 1-chloro-2-butanone in alkaline and neutral media is consistent with the intramolecular oxidation-reduction to acid in presence of metallic salts with or without addition of alkali. The susceptibility to reduction of 1-chloro-2-butanone, judging by all the polarographic data $(E_{1/2}, \frac{id}{c}, \alpha)$ exceeds that of 1-hydroxy-2-butanone, possibly due to the inductive effect of the chlorine atom.

No acidic transformation occurred in the case of the ketoalcohol with a primary alcohol group. On heating the chloroketone with 5% alkali solution and lead oxide, however, butyric acid was detected, although in low yield. The process may be represented by the equations:



$$CH_3-CH_2-CO-CH_2Cl \rightarrow CH_3CH_2\overset{O}{C}OH-CH_2 \rightarrow COOH-CH_2-CH_2-CH_3.$$

Publications by Favorsky [14] indicate that 3-chloro-2-butanone is converted into isobutyraldehyde in low yield.

Acidic products were not detected when 1-chloro-2-butanone was heated with sodium methoxide in anhydrous methyl alcohol.

According, however, to literature date [15], in the same conditions chloromethylbenzyl ketone $C_6H_5CH_2COCH_2Cl$ is completely converted into the ester of hydrocinnamic acid, while the primary chlorobenzylacetone $C_6H_5CH_2CH_2COCH_2Cl$ gives the corresponding acid in a yield of 8%. The aliphatic chloroketone $CH_3CH_2COCH_2Cl$ does not undergo the acidic transformation in presence of sodium ethoxide according to our experiments. We can, therefore, conclude that the phenyl radical favors the formation of acid from primary chloroketones.

It should be noted [16] that the acid transformation of chloroketones was developed in Favorsky's laboratory.

Previously proposed schemes of isomerization of α -hydroxyaldehydes via ketoalcohols with a primary alcohol group (the hypothesis of intermediate oxide-alcoholic forms [7] of Favorsky or that of intermediate dienols followed by allylic rearrangement [9] was used) must be modified in the light of the inability to obtain ketoalcohols with a primary alcoholic group on isomerization of α -hydroxyaldehydes; also they are not isomerized to alcohols with a secondary alcoholic group which are formed in experiments from α -hydroxyaldehydes.

Since the alcoholic-oxide scheme can be successfully applied to disubstituted glycolaldehydes, it is expedient to utilize for monosubstituted derivatives of glycolaldehyde, as was pointed out by E.D. Venus-Danilova and V.F. Kazimirova [9], a scheme according to which the α -hydroxyaldehyde changes into the dienol, which then undergoes the allylic rearrangement. Rejecting the primary ketoalcohol as an intermediate, we obtain such a scheme for the isomerization of monosubstituted glycolaldehydes:

$$R-CH_2-CHOH-CHO \rightarrow R-CH_2-COH=CHOH \rightarrow CH_2=COH-CHOH-R \rightarrow CH_3-CO-CHOH-R.$$

The transformation is effected in a weakly acid or weakly alkaline medium.

According to this scheme benzylglycolaldehyde must form phenylacetylcarbinol which is actually obtained by isomerization of the hydroxyaldehyde.

The proposed schemes, however, are only useful for a convenient representation of the transformations. Detailed kinetic studies are needed for clarification of the actual mechanism of the reactions in the conditions employed. Both in the cases considered and in other isomeric transformations we cannot exclude the probability (at least as a limiting case) of direct intramolecular rearrangement of the molecule under the influence of acid and alkali (hydrogen and hydroxyl ions) and heating [17].

EXPERIMENTAL

The primary and secondary chlorobutanones, hydroxybutanones and phenylacetol were synthesized for the experiments.

The chloroketones were prepared by chlorination of 2-butanone in a yield of 16% 1-chloro-2-butanone (b.p. 137 -138°, n_α^{20} 1.4311, d_4^{20} 1.0850) and 56% 3-chloro-2-butanone (b.p. 116-117°,). n_α^{20} 1.4210, d_4^{20} 1.0571). Properties and derivatives of the chlorobutanones have been described previously [12].

From the chloroketones were synthesized the corresponding ketoalcohols — 1-hydroxy-2-butanone from the primary and 3-hydroxy-2-butanone from the secondary chloroketone. The chloroketones were heated with absolutely dry potassium formate in a medium of anhydrous methanol; after fractionation in vacuum and in a stream of carbon dioxide, the ketoalcohol was obtained in a yield of 50%.

Preparation and Properties of 1-Hydroxy-2-butanone

We have already described this synthesis [12]. Here we give an example of a new modification of the synthesis.

A mixture of 60 g 1-chloro-2-butanone (b.p. 63° at 43 mm), 96 ml anhydrous methyl alcohol and 96 g dry potassium formate (m.p. 167°) was heated on a boiling water bath for 8 hours. The absolutely dry potassium formate was prepared by recrystallization from anhydrous ethyl alcohol and by prolonged drying in a vacuum pistolet over phosphorus pentoxide.

The reaction was carried out in a two-necked flask; in one neck was inserted a condenser closed with a calcium chloride tube; through the other neck was passed a stream of carbon dioxide. The end of the reaction was checked by a Beilstein test for halogen.

After termination of the heating, the liquid portion was filtered from the precipitate of potassium chloride which was washed with anhydrous ether. The ethereal extract was added to the main filtrate. After driving off the methyl formate (b.p. 32°)) and ether on a water bath and then (in vacuum) the methanol (b.p. 20-25° at 20 mm), the following fractions were isolated:

First fraction b.p. 54—56° (18 mm), 1.8 g 2nd fraction b.p. 56—60° (18 mm), 25.7 g; resinous residue 6.4 g.

Redistillation of the 2nd fraction in a carbon dioxide stream gave 23.5 g ketoalcohol with b.p. 58° at 18 mm, equivalent to 49%.

1-Hydroxy-2-butanone is a transparent, colorless liquid with a characteristic pleasant odor; it readily reduces Fehling solution in the cold.

B.p. 54° at 18 mm, 57° at 22 mm, 78° at 60 mm, 86° at 72 mm, 153—154° at 765 mm; d_4^{20} 1.0186; n_α^{20} 1.4237; n_D^{20} 1.4248; MR_α 22.03; MR_D 22.09. $C_4H_8O_2$. calculated MR_α 22.09; MR_D 22.21.

0.1533 g sub: 0.3075 g CO_2; 0.1253 g H_2O. 0.1639 g sub: 0.3288 g CO_2; 0.1353 g H_2O. Found %: C 54.74, 54.74; H 9.01, 9.29. $C_4H_8O_2$. Calculated %: C 54.54; H 9.09;

The osazone (m.p. 115°) and the p-nitrophenylhydrazone (m.p. 228°) of propionylcarbinol have been described before [12].

1-Hydroxy-2-butanone semicarbazone was prepared by mixing equimolecular amounts of aqueous solutions of ketoalcohol, semicarbazide hydrochloride and potassium carbonate. On standing, the semicarbazone does not come down. The water is evaporated in vacuum and the dry residue is extracted with hot chloroform. The chloroform extract deposits a white crystalline precipitate which after recrystallization from water has m.p. 66°, identical with that of the semicarbazone of 1-hydroxy-2-butanone obtained in these conditions by Kling [18]. From 0.5 g ketoalcohol was obtained, after recrystallization, 0.36 g semicarbazone.

0.0964 g substance: 24.5 ml N_2 (18°, 764 mm). Found%: N 29.05. $C_5H_{11}O_2N_3$. Calculated %: N 28.96.

The 2,4-dinitrophenylhydrazone. The products of interaction of 1-hydroxy-2-butanone with 2,4-dinitrophenylhydrazine have not been described in the literature. By reacting equimolecular amounts of 1-hydroxy-2-butanone and 2,4-dinitrophenylhydrazine we obtained a yellow powder, which after two recrystallizations from alcohol had m.p. 141-142°, and corresponded in analysis with the 2,4-dinitrophenylhydrazone of the ketoalcohol.

0.0962 g substance: 17.5 ml N_2 (79°, 761 mm). 0.1004 g substance: 18.0 ml N_2 (19°, 761 mm). Found % N 21.10, 20.79. $C_{10}H_{12}N_4$. Calculated %: N 20.87.

The 2,4-dinitrophenylosazone. On reacting 1-hydroxy-2-butanone with excess of 2,4-dinitrophenylhydrazine, an orange-red product is obtained which is insoluble in common organic solvents (alcohol, ethyl acetate, and pyridine). After digesting with alcohol and drying in a vacuum desiccator, a substance with m.p. 229-230° (0.70 g from 0.5 g ketoalcohol) is obtained; the analysis corresponds to the 2,4-dinitrophenylosazone of 1-hydroxy-2-butanone.

0.0937 g substance: 20.5 ml N_2 (19.5°, 760 mm). 4.190 mg substance: 0.9308 ml N_2 (18°, 735.6 mm). Found %: N 25.16, 5.24. $C_{16}H_{14}O_8N_8$. Calculated %: N 25.11.

Preparation and Properties of 3-hydroxy-2-butanone

3-Hydroxy-2-butanone was obtained by a slight modification of the above procedure for 1-hydroxy-2-butanone. 40 g 3-chloro-2-butanone, 64 g potassium formate, and 64 ml anhydrous methanol were placed in a glass tube, which was allowed to stand for 8 hours in an autoclave heated to 120°. After the usual working up and fractionation in a stream of carbon dioxide, 16.5 g of 3-hydroxy-2-butanone was obtained, equivalent to a yield of 51.6%.

3-Hydroxy-2-butanone is a colorless substance with a pleasant odor, which reduces Fehling solution in the cold.

B.p. 38° at 12 mm, 56° at 34 mm, 144° at 760 mm; n_D^{20} 1.4200; d_4^{20} 1.0101; MR_D 22.04. $C_4H_8O_2$. Calculated 22.21.

After a second distillation in vacuum, the pure substance starts to crystallize and in the course of a month it changes into a dense, white crystalline mass with m.p. 95° - the m.p. of the dimer of 3-hydroxy-2-butanone [19].

3-Hydroxy-2-butanone was converted by the usual method into the semicarbazone with m.p. 186-187° and the osazone with m.p. 243° in agreement with the melting points in the literature [20].

The p-nitrophenylhydrazone. Reaction of 3-hydroxy-2-butanone with an equimolecular amount of p-nitrophenylhydrazine gives a dark-red product which after recrystallization from a mixture of alcohol and pyridine has m.p. 246° and corresponds in analysis to 3-hydroxy-2-butanone p-nitrophenylhydrazone.

4.450 mg sub.: 0.7107 ml N_2 (20°, 754 mm). 2.855 mg sub.: 0.4510 ml N_2 (20°, 754 mm). Found %: N 18.46, 18.26. $C_{10}H_{13}O_3N_3$. Calculated %: N 18.83.

The 2,4-dinitrophenylhydrazone. Reaction of 2,4-dinitrophenylhydrazine with 0.5 g 3-hydroxy-2-butanone gave 1.27 g bright-orange powder which after recrystallization from a mixture of ethyl alcohol and ethyl acetate had m.p. 332° and corresponded in analysis to 3-hydroxy-2-butanone 2,4-dinitrophenylhydrazone, not described in the literature.

3.715 mg sub.: 0.670 ml N_2 (23°, 750 mm). 4.320 mg sub.: 0.789 ml N_2 (22°, 744 mm). Found %: N 20.60, 20.70. $C_{10}H_{12}O_5N_4$. Calculated %: N 20.87.

Experiments on Transformation of 1-Hydroxy-2-butanone

Experiments were run in the conditions selected by Danilov and Venus-Danilova [1] for transformation of α-hydroxyaldehydes; in no case, however, was the anticipated 3-hydroxy-2-butanone detected. For example, 1 g ketoalcohol was heated in an ampoule with 5 ml 1% sulfuric acid on a glycerol bath at 140-145° for 5.5 hours. The sulfuric acid was then neutralized with potassium acetate. The contents of the ampoule were poured into a solution of 4 g phenylhydrazine in 50% acetic acid. The resultant osazone melted at 115° and did not give a depression with the osazone obtained from 1-hydroxy-2-butanone. In these conditions, therefore, the hydroxyketone transformation does not take place.

Heating with salts of zinc, copper and lead (in aqueous and alkaline media) also gave only derivatives of 1-hydroxy-2-butanone and ethylglyoxal (osazone m.p. 115°, disemicarbazone m.p. 228°) [12], and no derivatives 3-hydroxy-2-butanone and 2,3-butanedione were detected. Nor was butyric acid detected.

Transformation of 1-chloro-2-butanone

Some of the experiments were described in our previous paper [12]. It has already been pointed out that heating to 100-150° of the primary chloroketone in an alkaline medium with lead oxide and in an aqueous medium with silver carbonate gave derivatives of the secondary ketoalcohol. We now add the further information that heating of 1-chloro-2-butanone for 10 hours in an ampoule on a water bath at 100° with lead oxide in an aqueous medium (15 g chloroketone, 40 g PbO_2 and 150 ml water) yielded (after steam distillation) neutral products giving, in addition to 1-hydroxy-2-butanone osazone with m.p. 115°, an osazone with m.p. 243° and the 2,4-dinitrophenylhydrazone of 3-hydroxy-2-butanone with m.p. 332°; the two latter derivatives did not give depressions with specimens synthesized from authentic 3-hydroxy-2-butanone. The dimer of 3-hydroxy-2-butanone with m.p. 95° was isolated at the same time.

After distilling off the neutral product with water until the reaction with Fehling's solution was negative, the salts remaining in the flask were washed with solvents (ether, chloroform, alcohol, benzene and acetone) to remove resin, and the pure residue of salts was acidified with 2% sulfuric acid; distillation was then continued. A distillate was obtained with a weakly acidic reaction which did not give a double-bond reaction with bromine; it had a weak odor of butyric acid. In one experiment, for example, after heating 14 g chloroketone in an ampoule with 30 g lead oxide and 200 ml 5% KOH solution to 140° for 10 hours, 0.35 g butyric acid was found (by titration with 0.1 N sodium hydroxide solution) in 300 ml acid distillate.

0.1024 g of silver butyrate was obtained.

0.0472 g salt: 0.0260 g Ag. 0.0532 g salt 0.0295 g Ag. Found %: Ag 55.08, 55.45. $C_4H_7O_2Ag$. Calculated %: Ag 55.38.

Preparation, Properties and Transformations of Phenylglycidol

Convenient syntheses of phenylacetol have not been described in the literature. We proposed to obtain this ketoalcohol by isomerization of the oxide of cinnamyl alcohol – phenylglycidol.

Phenylglycidol was prepared by oxidation [21] of cinnamyl alcohol with benzoyl hydroperoxide in solution in chloroform or carbon tetrachloride.

We give one example of the synthesis: To a solution of 45 g hydroperoxide in 1700 ml CCl_4 in a 3-liter flask cooled with ice was added, with intensive stirring, a solution of 15 g cinnamyl alcohol in 750 ml CCl_4. The reaction proceeded for a period of 24 hours. Its progress was checked by the bromine test for the double bond. The solution was washed with potassium carbonate and the greater proportion of the CCl_4 was driven off in vacuum. The residue was dried with ignited sodium sulfate. The remainder of the solvent was distilled off in vacuum, at first on a water bath from a small flask, and then in a vacuum desiccator.

The substance was obtained in the form of a syrupy, readily crystallizing liquid with a pleasant odor. It is insoluble in water, soluble in alcohol, ether, carbon tetrachloride and chloroform; it does not react with bromine or Fehling solution (even hot). Iodine is liberated when the substance is heated with potassium iodide in acetic acid. Heating with iron chloride brings down ferric hydroxide which dissolves readily in dilute acids. The phenylglycidol resinifies badly when distilled:

B.p. 138° at 3 mm; n_D^{27} 1.5432; d_4^{27} 1.1512; MR_D 41.08. $C_9H_{10}O_2$. Calculated 41.26 (Hibbert [21] gives for phenylglycidol b.p. 135° at 4 mm and n_D^{27} 1.5427)

0.1012 g sub.: 0.2670 g CO_2; 0.0606 g H_2O. 0.0965 g sub.: 0.2530 g CO_2; 0.0595 g H_2O. Found %: C 71.93, 71.60; H 6.62, 6.85 $C_9H_{10}O_2$. Calculated %: C 72.00; H 6.66.

The phenylurethane of phenylglycidol was prepared in the usual manner: m.p. 89-90° (Hibbert [21] gives m.p. 87°).

0.0846 g sub.: 3.5 ml N_2 (19° at 765 mm). 0.0998 g sub.: 4.5 ml N_2 (19°, 765 mm). Found %: N 4.87, 5.22. $C_{16}H_{15}O_3N$. Calculated %: N 5.20.

The conditions of isomerization of phenylglycidol to the ketoalcohol, phenylacetol, were not established. However, after heating 5 g phenylglycidol with 100 ml 1% aqueous sulfuric acid in an ampoule at 140° for 5 hours, followed by reaction with semicarbazide, a semicarbazone with m.p. 132-133° was isolated; Darmon [22] reported the same m.p. for phenylacetol semicarbazone. Since the above conditions are the same as those in which the isomerization of phenylglycolaldehyde to phenylacetylcarbinol was realized, and since the semicarbazone of the latter with m.p. 194° [7] was not isolated in our case, we can assume that phenylacetol does not isomerize to phenylacetylcarbinol in the given conditions.

SUMMARY

1. A study was made of the isomeric transformations of α-hydroxyaldehydes with reference to the role of α-ketoalcohols in oxidation-reduction processes.

2. It was shown that the primary ketoalcohols, 1-hydroxy-2-butanone and phenylacetol, do not isomerize in the conditions of transformations of α-hydroxyaldehydes. For this reason we may infer that the isomerization of α-hydroxyaldehydes to secondary ketoalcohols does not proceed via the primary ketoalcohol.

3. Heating of the primary chloroketone, 1-chloro-2-butanone, to 100° with silver carbonate or lead hydroxide (in an aqueous or alkaline medium) converts it into 1-hydroxy-2-butanone and 3-hydroxy-2-butanone.

4. Heating of 1-chloro-2-butanone to 140° with lead hydroxide in an aqueous alkaline medium gives butyric acid in 3% yield.

5. The data from experiments on isomerization were confirmed by the polarographic method, which showed the primary ketoalcohol to be less susceptible than the secondary ketoalcohol to reduction and also revealed the facility of reduction of the primary chloroketone.

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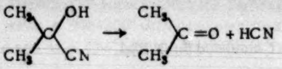
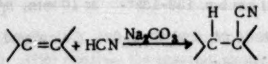
α-HYDROXYISOBUTYRONITRILE AS A SOURCE OF HYDROCYANIC ACID IN ADDITION REACTIONS

I.N. Nazarov and S.I. Zavyalov

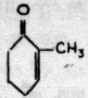
The addition of hydrocyanic acid to multiple bonds is effected, as we know, by means of liquid hydrocyanic acid or of cyanides of potassium and sodium, which, due to their high toxicity, are very inconvenient from the preparative standpoint. In this connection attention is deserving of the application of the simplest cyanohydrins in the synthesis of α-hydroxynitriles, starting from ketones [1, 2] and vinyl esters [3]. Although the addition of hydrocyanic acid to α,β-unsaturated olefinic compounds (ketones, aldehydes, nitriles, acids and their esters) has been exhaustively studied with reference to a great diversity of substances, there is no information at all in the literature regarding the possibility of utilization of the cyanohydrins of the simplest ketones in these reactions.

In the present investigation we showed that acetone cyanohydrin (α-hydroxyisobutyronitrile), in presence of an aqueous solution of sodium carbonate at 70-80° readily forms nitriles with various unsaturated compounds whose olefinic bond is activated by a carbonyl, nitrile or ester group. The reaction probably takes place in two stages: at first the α-hydroxyisobutyronitrile decomposes with release of free hydrocyanic acid, which then under the influence of sodium carbonate adds on to the active double bond:





In this manner 2-methyl-Δ^2-cyclohexene (I), 2-methyl-Δ^2-cyclopentenone (III) and 2,4-dimethyl-Δ^2-cyclopentenone (V) were converted into the ketonitriles (II), (IV) and (VI) in yields of 73, 77 and 55%, respectively.



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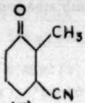

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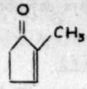

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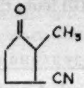

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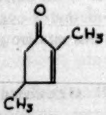

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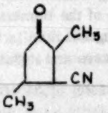

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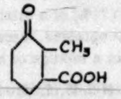

(VII)

The first two ketonitriles (II) and (IV) were isolated in the form of two stereoisomers, a liquid and a crystalline substance, which formed identical semicarbazones but different 2,4-dinitrophenylhydrazones. Since hydrolysis of the semicarbazones with hydrochloric acid gave the crystalline isomers, the latter in all probability possess the more stable trans-configuration. It is interesting to note that 2,4-dimethyl-Δ^2-cyclopentenone (V) forms only one isomer of 2,4-dimethyl-3-cyanocyclopentanone (VI). For confirmation of the structure of the obtained substances, both isomers of 2-methyl-3-cyanocyclohexanone (II) were converted by boiling with dilute caustic alkali into the known 2-methyl-3-ketocyclohexane carboxylic acid (VII). Reaction of acrylonitrile with α-hydroxyisobutyronitrile gives succinonitrile (VIII) in 88% yield, whereas with hydrocyanic acid [4] and potassium cyanide [5] the yields do not exceed 84%. Methyl acrylate proved to be considerably less reactive; with α-hydroxyisobutyronitrile it gives methyl β-cyanopropionate (IX) in a yield of only 50% after many hours' heating in a closed vessel.

$NCCH_2CH_2CN$ (VIII) $NCCH_2CH_2COOCH_3$. (IX)

We thus established that α-hydroxyisobutyronitrile can be used as a source of hydrocyanic acid not only for the synthesis of α-hydroxynitriles when starting from ketones, but also in other addition reactions.

The simplicity and convenience of the method and the mild reaction conditions make the cyanohydrin method of preparation of nitriles extremely valuable from the preparative standpoint.

EXPERIMENTAL

2-Methyl-3-Cyanocyclohexanone (II)

A mixture of 3 g 2-methyl-Δ^2-cyclohexenone (I) (b.p. 55-56° at 9 mm, n_D^{20} 1.4865) [6], 3 g α-hydroxyisobutyronitrile, 8 ml methanol and 0.2 g sodium carbonate in 3 ml water is heated under a reflux condenser on a water bath at 70-80° for 3 hours. After cooling, the reaction mixture is extracted with ether, the solvent is driven off, and the residue distilled in vacuum. Yield 2.7 g (73%) of a mixture of the isomers of 2-methyl-3-cyanocyclohexanone (II) with b.p. 134-138° at 10 mm.

Freezing and distillation of this mixture gave 0.5 g of the crystalline isomer (II) with m.p. 57-58 (from a mixture of benzene and ligroin).

Found %: C 69.80, 69.95; H 8.19, 8.22; N 10.20, 10.22. $C_8H_{11}ON$. Calculated %: C 70.1; H 8.0; N 10.2.

The semicarbazone melts at 223-225° with decomposition (from aqueous methanol).

Found %: N 28.65, 28.73. $C_9H_{14}ON_4$. Calculated %: N 28.7.
Hydrolysis of this semicarbazone with HCl gives the original cyanoketone (II) with m.p. 57-58°.
The 2,4-dinitrophenylhydrazone of the crystalline cyanoketone (II) melts at 208-209° (from aqueous methanol).

Found %: N 22.40, 22.55, $C_{14}H_{15}O_4N_5$. Calculated %: N 22.1.

The liquid isomer of the cyanoketone (II) has b.p. 136-138° at 10 mm; n_D^{20} 1.4725.

Found %: C 70.05, 69.94; H 8.18, 8.01; N 10.05, 9.98. $C_8H_{11}ON$. Calculated %: C 70.1; H 8.0; N 10.2.

Its 2,4-dinitrophenylhydrazone melts at 191-192° (from aqueous methanol) and gives a considerable depression with the 2,4-dinitrophenylhydrazone of the crystalline isomer.

Found %: N 22.19, 21.87. $C_{14}H_{15}O_4N_5$. Calculated %: N 22.1.

The liquid cyanoketone (II) forms the above-described semicarbazone of the crystalline isomer with m.p. 223-225°.

2-Methyl-3-cyanocyclopentanone (IV)

A mixture of 10 g 2-methyl-Δ^2-cyclopentenone (II) (b.p. 52-53° at 15 mm, n_D^{20} 1.4770) [6], 10 g α-hydroxyisobutyronitrile, 15 ml methanol and 0.5 g sodium carbonate in 10 ml water was refluxed for 3 hours. After working-up as above, 10 g (77%) of a mixture of the isomers of 2-methyl-3-cyanocyclopentanone (IV) with b.p. 88-89° at 2 mm was obtained. Freezing and distillation of this mixture gave 3 g of the crystalline isomer with m.p. 49-50° (from a mixture of benzene and ligroin).

Found %: C 67.79, 67.98; H 7.45, 7.53; N 11.30, 11.35. C_7H_9ON. Calculated %: C 68.2; H 7.3; N 11.3.

The semicarbazone melts at 226-227° with decomposition (from methanol).

Found %: 31.35, 31.48. $C_8H_{12}ON_4$. Calculated %: N 31.4.

Treatment with hydrochloric acid converts this semicarbazone into the original crystalline cyanoketone (IV) with m.p. 49-50°.

The 2,4-dinitrophenylhydrazone of the crystalline cyanoketone (IV) melts at 192-193° (from aqueous methanol).

Found %: N 23.15, 23.27. $C_{13}H_{13}O_4N_5$. Calculated %: N 23.1.

The liquid isomer of the cyanoketone (IV) has b.p. 88-89° at 2 mm; n_D^{22} 1.4617.

Found %: C 68.11, 68.38; H 7.53, 7.43; N 11.40, 11.60. C_7H_9ON. Calculated %: C 68.2; H 7.3; N 11.3.

Its 2,4-dinitrophenylhydrazone melts at 200-201° (from aqueous methanol) and gives a considerable depression with the 2,4-dinitrophenylhydrazone of the crystalline isomer.

Found %: N 23.25, 23.37. $C_{13}H_{13}O_4N_5$. Calculated %: N 23.1.

The liquid cyanoketone (IV) forms the above-described semicarbazone of the crystalline isomer with m.p. 226-227°.

2,4-Dimethyl-3-cyanocyclopentanone (VI)

The reaction is carried out as described above.

From 8 g 2,4-dimethyl-Δ^2-cyclopentenone (V) (b.p. 50-52° at 9 mm, n_D^{22} 1.4670) [6] was obtained 5 g (55%) 2,4-dimethyl-3-cyanocyclopentanone (VI) with b.p. 119-121° at 11 mm; n_D^{20} 1.4580.

Found %: C 69.97, 69.94; H 8.17, 8.21; N 10.08, 10.03. $C_8H_{11}ON$. Calculated %: C 70.1; H 8.0; N 10.2.

The semicarbazone melts at 204-206° with decomposition (from aqueous methanol).

Found %: N 28.55, 28.54. $C_9H_{14}ON_4$. Calculated %: N 28.7.

The 2,4-dinitrophenylhydrazone melts at 188-189° (from aqueous methanol).

Found %: N 22.38, 22.45. $C_{14}H_{15}O_4N_5$. Calculated %: N 22.1.

Hydrolysis of 2-methyl-3-cyanocyclohexanone

0.5 g of a mixture of the isomers of 2-methyl-3-cyanocyclohexanone (II) is boiled with a solution of 1.5 g KOH in 5 ml water for 7 hours. The cooled solution is acidified with dilute (1:1) hydrochloric acid until acid to congo and then extracted with chloroform. After driving off the solvent, the residue crystallizes almost completely. Yield 0.4 g (70%) 2-methyl-3-ketocyclohexane carboxylic acid (VII) with m.p. 96-97° (from n-hexane); the semicarbazone melts at 205-206° with decomposition (from aqueous methanol). The literature [7] reports m.p. 97° for this acid and m.p. 205° with decomposition for its semicarbazone.

Succinonitrile

A mixture of 5.3 g acrylonitrile, 9 g α-hydroxyisobutyronitrile and 0.5 g sodium carbonate in 3 ml water is refluxed at 70-75° for 3 hours. After cooling, the reaction product is extracted with chloroform and distilled in vacuum. Yield 7 g (88%) of succinonitrile (VIII) with b.p. 149-150° at 16 mm and m.p. 53-54° [5].

Methyl β-cyanopropionate

A mixture of 8.6 methyl acrylate, 9 g α-hydroxyisobutyronitrile and 0.5 g sodium carbonate in 8 ml water is heated in a sealed vessel at 70-80° for 15 hours. After cooling, the reaction product is extracted with ether and distilled at atmospheric pressure. Yield 5.6 g (50%) methyl β-cyanopropionate (IX) with b.p. 210-212°; n_D^{20} 1.4250.

The literature gives b.p. 215°; n_D^{20} 1.4243 [8].

SUMMARY

It is found that α-hydroxyisobutyronitrile can serve as a source of hydrocyanic acid in addition reactions at double bonds activated by carbonyl, nitrile and ester groups.

This method was used, starting from 2-methyl-Δ^2-cyclohexenone (I), 2-methyl-Δ^2-cyclopentenone (III), 2,4-dimethyl-Δ^2-cyclopentenone (V), acrylonitrile and methyl acrylate, to give respectively the nitriles (II), (IV), (VI), (VIII) and (IX) in yields of 73, 77, 55, 88, and 50% of the theoretical.

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CYANOETHYLATION OF CYCLIC β-DIKETONES

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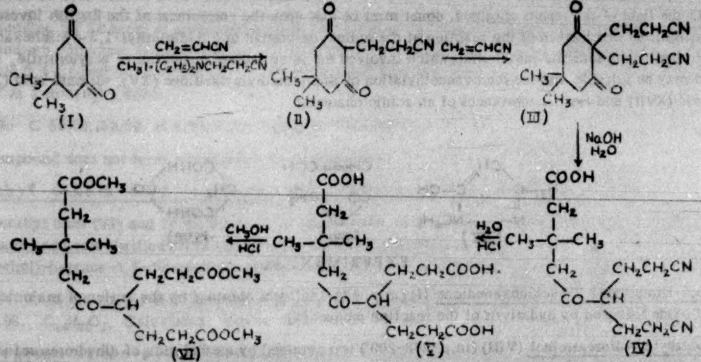
Following our discovery that cyclic β-diketones enter into addition reactions with various vinylketones [1], it seemed of interest to investigate the reaction of cyclic β-diketones with other unsaturated compounds, in particular acrylonitrile. The introduction of the cyanoethyl group into the dihydroresorcinol (XIII) molecule and its derivatives should permit access to various difficultlyaccessible organic compounds of the aliphatic, cyclic and heterocyclic series.

A number of American [2 3] and English investigators [4] have attempted to effect the cyanoethylation of dihydroresorcinol (XIII), 5,5-dimethyl-1,3-cyclohexanedione (i.e. dimedon) (I) and similar compounds but were unsuccessful. These authors reached the conclusion that cyclic β-diketones in general cannot enter into addition reactions with acrylonitrile. This assertion has proved erroneous since we have shown that 5,5-dimethyl-1,3-cyclohexanedione (I), methyldihydroresorcinol (VIII) and dihydroresorcinol (XIII) in presence of aqueous NaOH at 100° readily and completely react with acrylonitrile to form various addition products, depending on the structure of the β-diketone, the amount of alkali and the reactants used.

Reaction of 5,5-dimethyl-1,3-cyclohexanedione (I) with excess of acrylonitrile in presence of one equivalent of alkali leads to formation of mono- and bis-adducts (II) and (III) together with a considerable amount of the dicyanoketoacid (IV) formed from the bis-adduct (III) by hydrolytic cleavage of the dihydroresorcinol ring. Hydrolysis of the dicyanoketo acid (IV) gives 2,2-dimethyl-4-keto-5-(2'-carboxethyl)-heptane-1,7-dicarboxylic acid (V) which with a methanol solution of hydrogen chloride forms the trimethyl ester (VI). The structure of the prepared compounds was confirmed by special experiments which showed that in the above-specified conditions (β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (II) is transformed into the bis-adduct (III) and the latter into the keto acid (IV).

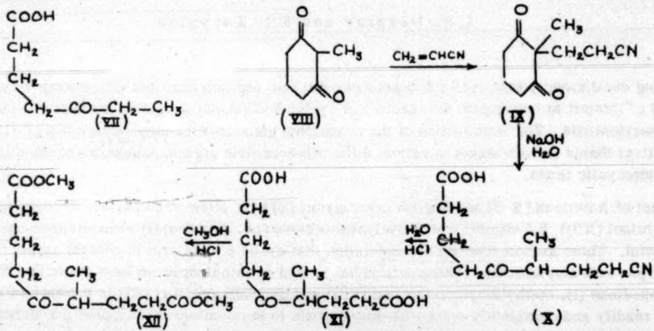
When using 1/6 equivalent of alkali and excess of acrylonitrile, the cyanoethylation of 5,5-dimethyl-1,3-cyclohexanedione (I) gives mainly the bis-adduct (III). The melting point of (β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (II) exactly coincides with that of the substance obtained by English investigators [4] from the sodium derivative of 5,5-dimethyl-1,3-cyclohexanedione and β-diethylaminopropionitrile methiodide.



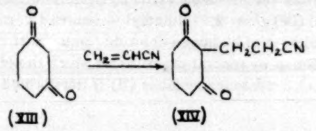
Heating of methyldihydroresorcinol (VIII) with acrylonitrile in an aqueous dioxane medium in presence of an equivalent of caustic alkali leads exclusively to the cyanoketo acid (X) which is formed by hydrolytic cleavage of (β-cyanoethyl)-methyldihydroresorcinol (IX). The suggestion that hydrolytic cleavage of methyldihydroresorcinol (VIII) itself to γ-propionylbutyric acid (VII) takes place during the reaction, followed by cyanoethylation of the latter, was not confirmed, since the authentic keto acid (VII) in the same conditions does not react with acrylonitrile.

On hydrolysis, the cyanoketo acid (X) is transformed into 4-keto-5-methylheptane-1,7-dicarboxylic acid (XI) which forms the dimethyl ester (XII) under the action of methanol in presence of hydrogen chloride.

In presence of 1/6 equivalent of NaOH the cyanoethylation of methyldihydroresorcinol leads in good yield to the normal product of addition (IX) which actually proved very sensitive to the action of alkali and readily underwent cleavage to form the above-mentioned keto acid (X).

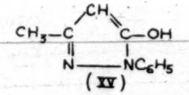


The cyanoethylation of dihydroresorcinol (XIII) is a more complex process. Individual products of the reaction could not be isolated when using 1/6 equivalent of alkali, but a mixture of compounds from which (β-cyanoethyl)-dihydroresorcinol (XIV) was isolated was formed when using an equivalent of alkali.



The cyanoethylation of cyclic β-diketones also proceeds at temperatures below 100°. In these conditions, however, the reaction velocity is considerably reduced. Thus, for example, 5,5-dimethyl-1,3-cyclohexanedione when heated with excess of acrylonitrile at 60-70° in an aqueous dioxane medium in presence of 1/6 equivalent of alkali gave only the monocyanoethyl derivative in a yield of 56%.

In the light of the results obtained, doubt must be cast upon the correctness of the English investigators' [4] hypothesis of the mechanism of the reaction of the sodium derivative of 5,5-dimethyl-1,3-cyclohexanedione with β-diethylaminopropionitrile methiodide, which involved the intermediate formation of acrylonitrile. Our own method may be suitable also for the cyanoethylation of phenylmethylpyrazolone (XV), tetronic acid (XVI), barbituric acid (XVII) and similar substances of an acidic character.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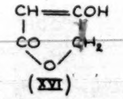
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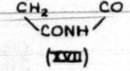
(XVII)

EXPERIMENTAL

5,5-Dimethyl-1,3-cyclohexanedione (I) (m.p. 144-145°) was obtained by the action of malonic ester on mesityl oxide followed by hydrolysis of the reaction product [5].

Methyldihydroresorcinol (VIII) (m.p. 208-209°) was obtained by methylation of dihydroresorcinol [1].

Dihydroresorcinol (XIII) (m.p. 104-105°) was prepared by hydrogenation of resorcinol [6].

Cyanoethylation of 5,5-dimethyl-1,3-cyclohexanedione

1. To a solution of the Na-derivative of 5,5-dimethyl-1,3-cyclohexanedione (I), prepared from 0.8 g NaOH, 5 ml water and 2.8 g 5,5-dimethyl-1,3-cyclohexanedione, was added 4 g acrylonitrile in 8 ml dioxane. The mixture was refluxed for 1.5 hours.

Evaporation of the solution in vacuum gave 1.1 g di-(β-dicyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (III) with m.p. 146-147° (from aqueous methanol).

Found %: C 68.55, 68.40; H 7.50, 7.30; N 11.43, 11.53. $C_{14}H_{18}O_2N_2$. Calculated %: C 68.2; H 7.3; N 11.4.

Acidification of the alkaline mother liquor with conc. hydrochloric acid followed by extraction with chloroform gave 3.8 g viscous oil which partially crystallized after addition of ether. Yield 0.5 g (β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (II) with m.p. 151-152° (from water).

Found %: C 68.46, 68.55; H 8.11, 8.04; N 7.19, 7.30. $C_{11}H_{15}O_2N$. Calculated %: C 68.4; H 7.8; N 7.3.

On standing, the mother liquor crystallized almost completely to give 1.5 g dicyanoketo acid (IV) with m.p. 62-63° (from a mixture of ether and n-hexane).

Found%: C 63.61, 63.72; H 8.04, 7.86; N 10.30, 10.24. $C_{14}H_{20}O_3N_2$. Calculated %: C 63.6; H 7.6; N 10.6.
Found: equiv (titration) 260, 262. $C_{14}H_{20}O_3N_2$. Calculated: equiv. 264.

2. To a solution of 0.07 g NaOH in 5 ml of water was added 1.4 g 5,5-dimethyl-1,3-cyclohexane dione (I) and then 3 g acrylonitrile in 5 ml dioxane. The mixture was refluxed for 3.5 hours. Evaporation of the solution brought down 2 g (81%) crystals with m.p. 146-147° (from aqueous methanol), which did not give a depression with the above-described bis-adduct (III).

3. To a solution of 0.025 g NaOH in 3 ml water was added 0.5 g 5,5-dimethyl-1,3-cyclohexane dione and 2 g acrylonitrile in 3 ml dioxane. The mixture was heated at 60-70° for 5 hours. On evaporation of the solution in vacuum 0.4 g (56%) of the mono-adduct (II) came down; m.p. 150-152° (from water).

Hydrolytic Cleavage of Di-(β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione.

A mixture of 0.5 g of (III), m.p. 146-147°, and 1 g potassium carbonate in 10 ml water was refluxed for 15 minutes. Acidification of the solution with conc. HCl and extraction with chloroform gave 0.4 g (74%) dicyanoketo acid (IV), m.p. 62-63° (from a mixture of ether and n-hexane). Hydrolytic cleavage of (III) also occurs in alkali.

Transformation of (II) into the bis-Adduct (III)

To a solution of 0.023 g NaOH in 8 ml water were added 0.5 g (β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (II) with m.p. 151-152° and 2 g acrylonitrile in 5 ml dioxane. The mixture was refluxed for 2 hours. On evaporation of the solution in vacuum, 0.4 g (59%) crystals with m.p. 146-147° (from aqueous methanol) came down; they did not give a depression with the dicyanoethyl derivative (III).

Trimethyl 2,2-dimethyl-4-keto-5-(2'-carboxethyl)-heptane-1,7-dicarboxylate

2.6 g dicyanoketo acid (IV) with m.p. 62-63° and 30 ml dilute (1:1) hydrochloric acid were refluxed for 6 hours. The solution was evaporated to dryness in vacuum; the residual crude tricarboxylic acid (V) was dissolved in acetone to free it from ammonium chloride; after driving off the solvent, it was mixed with 50 ml saturated solution of hydrochloric acid in methanol.

After standing for 24 hours at room temperature, the solution was evaporated in vacuum; the residue was treated with sodium carbonate solution and the reaction product was extracted with ether and fractionated in vacuum. Yield 2.4 g trimethyl 2,2-dimethyl-4-keto-5-(2'-carboxethyl)-heptane-1,7-dicarboxylate (VI) with b.p. 187-189° at 1 mm; n_D^{22} 1.4584.

Found %: C 59.02, 59.02; H 8.20, 8.30. $C_{17}H_{28}O_7$. Calculated %: C 59.2; H 8.1.

The compound does not form a crystalline semicarbazone or 2,4-dinitrophenylhydrazone.

2,2-Dimethyl-4-keto-5-(2'-carboxethyl)-heptane-1,7-dicarboxylic acid

1 g trimethyl ester (VI) and 10 ml dilute (1:1) hydrochloric acid were refluxed for 6 hours. After the volatile products had been distilled off in vacuum, the residue crystallized. Yield 0.6 g 2,2-dimethyl-4-keto-5-(2'-carboxethyl)-heptane-1,7-dicarboxylic acid (V), m.p. 109-110° (from a mixture of benzene and dioxane).

Found %: C 55.53, 55.71; H 7.12, 7.23. $C_{14}H_{22}O_7$. Calculated %: C 55.6; H 7.3. Found: equiv. (titration) 96.98. $C_{14}H_{22}O_7$. Calculated: equiv. 100.7.

Cyanoethylation of methyldihydroresorcinol

1. To a solution of the sodium derivative of methyldihydroresorcinol (VIII) prepared from 0.9 g NaOH, 5 ml water and 3 g diketone was added 4 g acrylonitrile in 8 ml dioxane. The mixture was refluxed for 3 hours. Acidification and extraction of the solution with chloroform gave 3.5 g (74%) of the cyanoketo acid (X) with b.p. 200-203° at 2 mm; n_D^{20} 1.4763.

Found %: C 61.12, 61.12, H 8.06, 7.95; N 7.50, 7.65. $C_{20}H_{15}O_3N$. Calculated %: C 60.9; H 7.7; N 7.2. Found: equiv. (titration) 194, 196. $C_{10}H_{15}O_3N$. Calculated: equiv. 197.

The substance does not form a crystalline semicarbazone or 2,4-dinitrophenylhydrazone.

2. To a solution of 0.1 g NaOH in 8 ml water were added 2 g methyldihydroresorcinol (VIII) and 4 g acrylonitrile in 5 ml dioxane. The mixture was refluxed for 3 hours and then extracted with ether. After the solvent had been driven off, the residue was distilled in vacuum to give 2.3 g (82%) (β-cyanoethyl)-methyldihydroresorcinol (IX) with b.p. 142-144° at 1 mm; n_D^{20} 1.4890.

Found %: C 67.13, 67.05; H 7.21, 7.24; N 8.16, 8.22. $C_{10}H_{13}O_2N$. Calculated %: C 67.0; H 7.3; N 7.8.

Hydrolytic cleavage of (β-cyanoethyl)-methyldihydroresorcinol

A mixture of 3 g (β-cyanoethyl)-methyldihydroresorcinol (IX) and 1 g NaOH in 20 ml water was refluxed for one-half hour. Acidification followed by extraction with chloroform gave 2.5 g cyanoketo acid (X) with b.p. 200-202° at 2 mm; n_D^{20} 1.4760.

Dimethyl 4-keto-5-methylheptane-1,7-dicarboxylate

2 g cyanoketo acid (X) in 30 ml dilute (1:1) hydrochloric acid was refluxed for 6 hours. The solution was evaporated to dryness in vacuum; the residual dicarboxylic acid (XI) was freed from ammonium chloride as described above and mixed with a saturated methanol solution of hydrochloric acid (20 ml). After standing for 24 hours at room temperature, the solution was evaporated to dryness; the residue was treated with sodium carbonate solution and the reaction product was extracted with ether and distilled to give 1.8 g dimethyl 4-keto-5-methylheptane-1,7-dicarboxylate (XII) with b.p. 142-144° at 2 mm, n_D^{22} 1.4473.

Found %: C 58.77, 58.72; H 7.97, 8.11, $C_{12}H_{20}O_5$. Calculated %: C 59.0; H 8.2

The compound does not give a crystalline semicarbazone or 2,4-dinitrophenylhydrazone.

Hydrolysis with dilute hydrochloric acid of the dimethyl ester (XII) gave the oily dicarboxylic acid (XI) which failed to crystallize.

Cyanoethylation of dihydroresorcinol

1. To a solution of the Na derivative of dihydroresorcinol (XIII), prepared from 1.2 g NaOH, 8 ml water and 3.5 g diketone was added 5 g acrylonitrile in 10 ml dioxane. After refluxing for 2.5 hours, the solution was acidified with conc. hydrochloric acid and extracted with chloroform to give 1.2 g (23%) (β-cyanoethyl)-dihydroresorcinol (XIV) with m.p. 203-204° (from water).

Found %: C 65.17, 65.10; H 6.77, 6.68; N 8.91, 8.90. $C_9H_{11}O_2N$. Calculated %: C 65.4; H 6.77; N 8.5.

2. To a solution of 0.05 g NaOH in 5 ml water were added 1.4 g dihydroresorcinol (XIII) and 4 g acrylonitrile in 3 ml dioxane. The mixture was refluxed for 6 hours. On cooling, 2 g white powder came down; it decomposed at 190-200° and was insoluble in water and organic solvents.

SUMMARY

1. The incorrectness was shown of the claims of some American and English investigators that cyclic β-diketones are not amenable to cyanoethylation.

2. A method was discovered for cyanoethylation of cyclic β-diketones consisting in heating with acrylonitrile at 100° in an aqueous dioxane medium in presence of caustic alkali.

3. Reaction of 5,5-dimethyl-1,3-cyclohexanedione (I) with acrylonitrile leads to good yields of (β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (II), di-(β-cyanoethyl)-5,5-dimethyl-1,3-cyclohexanedione (III) and a dicyanoketo acid (IV).

4. Cyanomethylation of methyldihydroresorcinol (VIII) gives (β-cyanoethyl)-methyldihydroresorcinol (IX) and a cyanoketo acid (X) in a yield of about 80%.

5. Cyanoethylation of dihydroresorcinol (XIII) gave (β-cyanoethyl)-dihydroresorcinol (XIV) in a yield of 23%.

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ESTERS OF ARYLSULFONIMIDOPHOSPHORIC ACIDS

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In recent years [1] trichlorophosphazosulfonaryls have become easily accessible substances. They are exceptionally reactive and can serve as starting materials for the preparation of a large number of compounds of the most diverse types.

In previous papers [2] results were reported of a study of the hydrolysis and acidolysis of trichlorophosphazosulfonaryls, and the products of reaction of trichlorophosphazosulfonaryls with ammonia and aromatic amines were described.

In the present paper are communicated the results of a study of reactions of trichlorophosphazosulfonaryls with sodium alkoxides, and the resultant aliphatic esters of arylsulfonimidophosphoric acids are described. In addition, the synthesis and properties of α- and β-trichlorophosphazosulfonnaphthyls are described.

On slowly running a benzene solution of trichlorophosphazosulfonaryl into a solution of sodium alkoxide in the corresponding alcohol with thorough stirring and cooling with iced water, the full esters of the arylsulfonimidophosphoric acids can be obtained in a yield of 70-80%. The trialkyl esters of the arylsulfonimidophosphoric acids are formed according to the scheme:

$$\mathrm{ArSO_2N{=}PCl_3 + 3AlkONa \rightarrow ArSO_2N{=}P(OAlk)_3 + 3NaCl.}$$

Always accompanying the full esters as secondary products are the dialkyl esters of arylsulfonamidophosphoric acids. Formation of the latter is explained either by interaction of the full esters with still unreacted sodium alkoxide

$$\mathrm{ArSO_2N{=}P(OAlk)_3 + AlkONa \longrightarrow ArSO_2NNaPO(OAlk)_2 + AlkOAlk,}$$

or (less probably) by direct reaction according to the scheme:

$$\mathrm{ArSO_2N{=}PCl_3 + 3AlkONa \longrightarrow ArSO_2NNa{-}PO(OAlk)_2 + AlkCl + 2NaCl.}$$

The yield of dialkyl esters is 10-20%. The total yield of trialkyl and dialkyl esters is 90-95%.

Reaction of trichlorophosphazosulfonaryls with sodium alkoxides gives, in addition to trialkyl and dialkyl esters, small quantities of by-products of unknown structure which impart to the reaction mixture and to the crude, unpurified products an extraordinarily unpleasant odor.

Reaction of trichlorophosphazosulfonaryls with sodium alkoxides gave the trimethyl, triethyl and tri-n-butyl esters of phenyl-, o- and p-tolyl, and α- and β-naphthylsulfonimidophosphoric acids. Secondary products were the corresponding dialkyl esters.

The tri- and dialkyl esters obtained are set forth in Table 1.

The trialkyl esters are colorless crystalline substances or viscous, oily liquids; they are tasteless and odorless. The triethyl and trimethyl esters are very readily soluble in acetone, benzene, and chloroform, readily soluble in ether, hot alcohol and hot carbon tetrachloride. The tri-n-butyl esters are miscible in all proportions with the above solvents. The trialkyl esters are insoluble in water.

The trimethyl and the solid triethyl esters readily crystallize from ether, carbon tetrachloride and alcohol.

Distillation at atmospheric pressure decomposes the trialkyl esters, but they distil without decomposition in vacuum.

Chemically the full esters of arylsulfonimidophosphoric acids are stable and neutral substances. They are perfectly stable to water and do not react with it even after prolonged heating. They are also stable toward dilute mineral acids at room temperature but at the boil they are hydrolyzed, although very slowly. Thus, heating at the boil for an hour of 0.001 mole full ester with 25 ml 0.2 N aqueous hydrochloric acid caused no change in the ester and it could be recovered to the extent of 95%. The stability of the full esters of arylsulfonimidophosphoric acids toward weak aqueous solutions of mineral acids is evidently explicable by their insolubility in water. Actually, if in place of an aqueous solution, we take a 0.2 N aqueous alcoholic solution of hydrochloric acid (5 ml 1 N aqueous solution of acid + 20 ml alcohol), in which the full esters are readily soluble, then on

TABLE 1

Trialkyl Esters of Arylsulfonimidophosphoric Acids and Dialkyl Esters of Arylsulfonamidophosphoric Acids

Formula of prepared ester	Yield (in %)	Melting point
$C_6H_5SO_2N=P(OCH_3)_3$	75.9	38-40°
$C_6H_5SO_2NHPO(OCH_3)_2$	15.1	108-109
o-$CH_3C_6H_4SO_2N=P(OCH_3)_3$	76.0	74-75
o-$CH_3C_6H_4SO_2NHPO(OCH_3)_2$	20.4	145-146
p-$CH_3C_6H_4SO_2N=P(OCH_3)_3$	80.5	44-45
p-$CH_3C_6H_4SO_2NHPO(OCH_3)_2$	8.9	110-111
α-$C_{10}H_7SO_2N=P(OCH_3)_3$	71.7	84-85
α-$C_{10}H_7SO_2NHPO(OCH_3)_2$	25.1	164-165
β-$C_{10}H_7SO_2N=P(OCH_3)_3$	79.6	93-94
β-$C_{10}H_7SO_2NHPO(OCH_3)_2$	12.7	144-145
$C_6H_5SO_2N=P(OC_2H_5)_3$	81.5	Liquid
$C_6H_5SO_2NHPO(OC_2H_5)_2$	6.8	111-112
o-$CH_3C_6H_4SO_2N=P(OC_2H_5)_3$	82.1	35-37
o-$CH_3C_6H_4SO_2NHPO(OC_2H_5)_2$	9.7	97-98
p-$CH_3C_6H_4SO_2N=P(OC_2H_5)_3$	78.7	Liquid
p-$CH_3C_6H_4SO_2NHPO(OC_2H_5)_2$	7.8	105-106
α-$C_{10}H_7SO_2N=P(OC_2H_5)_3$	86.4	94-95
α-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	8.16	154-155
β-$C_{10}H_7SO_2N=P(OC_2H_5)_3$	75.4	51-52
β-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	20.4	161-162
$C_6H_5SO_2N=P(OC_4H_9\text{-n.})_3$	85.1	Liquid
o-$CH_3C_6H_4SO_2N=P(OC_4H_9\text{-n.})_3$	88.7	
α-$C_{10}H_7SO_2N=P(OC_4H_9\text{-n.})_3$	86.9	
β-$C_{10}H_7SO_2N=P(OC_4H_9\text{-n.})_3$	90.9	

TABLE 2

Hydrolysis of 0.001 mole of full Esters of Arylsulfonimidophosphoric acids with 0.2 N Aqueous Alcoholic Hydrochloric Acid

In the course of an hour

Formula of ester subjected to hydrolysis	Amount of unreacted ester		Yield of dialkyl ester	
	(in g)	(in %)	(in g)	(in %)
$C_6H_5SO_2N=P(OCH_3)_3$	0	0	0.19	71.7
o-$CH_3C_6H_4SO_2N=P(OCH_3)_3$	0	0	0.20	71.6
α-$C_{10}H_7SO_2N=P(OCH_3)_3$	0	0	0.30	95.1
β-$C_{10}H_7SO_2N=P(OCH_3)_3$	0	0	0.29	92.0
$C_6H_5SO_2N=P(OC_2H_5)_3$	0.14	43.6	0.15	51.1
o-$CH_3C_6H_4SO_2N=P(OC_2H_5)_3$	0.18	53.7	0.11	35.8
α-$C_{10}H_7SO_2N=P(OC_2H_5)_3$	0.23	61.9	0.10	29.1
β-$C_{10}H_7SO_2N=P(OC_2H_5)_3$	0.17	45.8	0.17	49.5
α-$C_{10}H_7SO_2N=P(OC_4H_9)_3$	0.30	66.7	Not determined	

heating to the boil for an hour the full methyl esters are completely hydrolyzed; the ethyl and butyl esters are less easily hydrolyzed. Thus the tri-n-butyl ester of α-naphthylsulfonimidophosphoric acid is only hydrolyzed to the extent of 33.3% when boiled for an hour with 0.2 N aqueous alcoholic solution of hydrochloric acid.

The yields of products of hydrolysis of the full esters of arylsulfonimidophosphoric acids with a 0.2 N aqueous alcoholic solution of hydrochloric acid are set forth in Table 2.

Short-period boiling of esters of arylsulfonimidophosphoric acids with aqueous alcoholic hydrochloric acid causes the hydrolysis to proceed mainly to the first stage with formation of dialkyl esters according to the scheme:

$$ArSO_2N=P(OAlk)_3 + H_2O \xrightarrow{H^+} ArSO_2NHPO(OAlk)_2 + AlkOH.$$

Realization of the second stage of hydrolysis with the aim of obtaining the monoalkyl esters was not possible. Hydrolysis always yielded the arylsulfamides.

Hydrolysis of trialkyl esters of arylsulfonimidophosphoric acids in an alkaline medium proceeds very much more easily and quickly than the hydrolysis of the same esters in an acid medium; in these conditions hydrolysis always leads to salts of the dialkyl esters:

$$ArSO_2N{=}P(OAlk)_3 + NaOH \rightarrow ArSO_2NNa{-}PO(OAlk)_2 + AlkOH.$$

In aqueous solutions of alkali, however, hydrolysis proceeds very slowly, apparently due to the same reason as the slowness of hydrolysis in aqueous solutions of mineral acids, i.e. the poor solubility of the full esters in water.

An exception is the trimethyl ester of phenylsulfonimidophosphoric acid, which when shaken with 1 N aqueous solution of NaOH is wholly converted after only 30 minutes at room temperature into the sodium salt of the dimethyl ester:

$$C_6H_5SO_2N{=}P(OCH_3)_3 + NaOH \rightarrow C_6H_5SO_2NNa{-}PO(OCH_3)_2 + CH_3OH.$$

In aqueous-alcoholic solution of NaOH the hydrolysis proceeds easily and quickly in the case of all the full esters. Thus, on heating on a water bath 0.001 -mole of trialkyl esters of arylsulfonimidophosphoric acids with 0.2 N aqueous alcoholic NaOH (5 ml 1 N aqueous solution of NaOH + 20 ml alcohol), hydrolysis takes place quantitatively in 1 hour.

Neither dilute nor concentrated solutions of alkalies, nor sodium ethoxide, hydrolyze the trialkyl esters beyond the stage of formation of salts of dialkyl esters.

In ths respect trialkyl esters of arylsulfonimidophosphoric acids resemble the esters of monobasic mineral acids, for example triethyl phosphate, diethyl sulfate and diethyl carbonate, which only undergo hydrolysis of one ester group in alkaline solution [3].

Yields of hydrolysis products are set forth in Table 3.

TABLE 3

Yield of Dialkyl Esters of Arylsulfcnamidophosphoric Acids on Hydrolysis of 0.001 -mole of the full Esters with Aqueous-Alcoholic Solution of Sodium Hydroxide

Formula of ester subjected to hydrolysis	Yield of dialkyl ester (in g)	Yield of dialkyl ester (in %)	Melting Point
$C_6H_5SO_2N{=}P(OCH_3)_3$	0.26	93.1	108-109°
α-$C_{10}H_7SO_2N{=}P(OCH_3)_3$	0.30	95.1	164-165
β-$C_{10}H_7SO_2N{=}P(OCH_3)_3$	0.29	92.0	144-145
o-$CH_3C_6H_4SO_2N{=}P(OC_2H_5)_3$	0.27	96.7	97-98
α-$C_{10}H_7SO_2N{=}P(OC_2H_5)_3$	0.33	96.1	154-155
β-$C_{10}H_7SO_2N{=}P(OC_2H_5)_3$.	0.33	96.1	161-162
α-$C_{10}H_7SO_2N{=}P(OC_4H_9)_3$.	0.37	92.5	75-77

On the basis of the observation that trialkyl esters are easily and completely hydrolyzed to dialkyl esters in alkali solutions, it may be suggested that dialkyl esters should be obtainable in good yield directly from trichlorophosphazosulfonaryls if 4 moles or more of sodium alkoxides and not 3, are introduced into the reaction for each -mole trichlorophosphazosulfonaryl.

Actually, if a benzene solution of 0.01 mole trichlorophosphazosulfonaryl is run with stirring into a solution of sodium alkoxide, taken in excess (0.045 -mole), then the sodium salt of the dialkyl ester is formed according to the scheme:

$$ArSO_2N{=}PCl_3 + 3AlkONa \rightarrow 3NaCl + ArSO_2N{=}P(OAlk)_3.$$

$$ArSO_2N{=}P(OAlk)_3 + AlkONa \rightarrow ArSO_2NNa{-}PO(OAlk)_2 + AlkOAlk.$$

Acidification of the aqueous solutions of the sodium salts of the dialkyl esters brings down the difficultly soluble free dialkyl esters whose properties are identical with those of the dialkyl esters obtained as secondary products in the synthesis of trialkyl esters or in the alkaline hydrolysis of trialkyl esters (see above). The dialkyl esters obtained in this way are set forth in Table 4.

TABLE 4

Yield of Dialkyl Esters of Arylsulfonamidophosphoric Acids when Prepared Directly from 0.01 mole of Trichlorophosphazosulfonaryls

Formula of dialkyl ester	Yield		Melting Point
	(in g)	(in %)	
$C_6H_5SO_2NHPO(OCH_3)_2$	2.37	89.4	108-109°
p-$CH_3C_6H_4SO_2NHPO(OCH_3)_2$	2.27	74.0	110-111
a-$C_{10}H_7SO_2NHPO(OCH_3)_2$	2.91	92.3	164-165
p-$CH_3C_6H_4SO_2NHPO(OC_2H_5)_2$	2.53	82.4	105-106
a-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	3.07	89.6	154-155

The dimethyl and diethyl esters of arylsulfonamidophosphoric acids are colorless crystalline compounds. In comparison with the full esters they all possess relatively high melting points; they crystallize nicely from water or dilute alcohol. The dimethyl and diethyl esters are readily soluble in acetone, chloroform, dichloroethane, hot alcohol and boiling benzene; the dialkyl esters are difficulty soluble in ether, ligroin, carbon tetrachloride, cold benzene and cold water.

Chemically the dialkyl esters are monobasic acids which displace carbonic and acetic acid from their salts. They titrate with sodium hydroxide to exactly one equivalent (using phenolphthalein as indicator).

The dibutyl esters of arylsulfonamidophosphoric acids are viscous liquids with the exception of the readily crystallizable dibutyl ester of a-naphthylsulfonamidophosphoric acid.

EXPERIMENTAL

Reaction of Trichlorophosphazosulfonaryls with a Solution of Sodium Methoxide in Methyl Alcohol

Into a three-necked flask of 150 ml capacity, fitted with reflux condenser, thermometer and dropping funnel, is introduced 15 ml anhydrous methanol, and addition is made of 0.7 g (0.03 mole) metallic sodium. After all the sodium has dissolved, the reflux condenser is replaced by a stirrer.

The mass is cooled with ice water; with energetic stirring, a solution of 0.01 -mole trichlorophosphazosulfonaryl in 30 ml dry benzene is run in at such a speed (20-30 minutes) that the temperature of the reaction mixture does not rise above 5°. When the mixing of the reacting solutions is completed, the sodium chloride is drained off at the pump and washed with methanol. The filtrate is evaporated and the benzene and alcohol are distilled off on a boiling water bath. The residue is a viscous, oily liquid to which is added 30 ml water. After thorough shaking, the sodium salts of the acid esters of the arylsulfonamidophosphoric acids go into solution while the water-insoluble trimethyl esters of arylsulfonimidophosphoric acids generally come down in the crystalline state. The crystal mass is drained off, well washed with water, and recrystallized.

The trimethyl esters of phenyl- and p-tolylsulfonimidophosphoric acids have a relatively low melting point so that treatment of the reaction mixture with water causes them to separate as a heavy oily layer. They are isolated by extraction of the aqueous mixture with benzene. The benzene extract is washed with water, filtered and dried with sodium sulfate; the benzene is driven off in vacuum on a boiling water bath. The residual light-yellow, oily liquid readily crystallizes on cooling with iced water and rubbing with a glass rod.

The yield of full methyl esters of arylsulfonimidophosphoric acids is 70-80%.

If the aqueous solutions are made acid to congo with hydrochloric acid after separation of the full methyl esters, the dimethyl esters of the arylsulfonamidophosphoric acids come down either at once in the crystalline form or, more often, as a heavy, oily layer which easily crystallizes when rubbed with a glass rod. The yield of dimethyl esters is 15-20%.

By this method were obtained the following esters.

Trimethyl phenylsulfonimidophosphate. Yield 2.12 g (75.9%). The crude product was purified by pressing between filter paper and crystallizing from slowly evaporating ethyl ether. Large, well-formed prisms, m.p. 30-40°.

0.0284 g sub.: 1.256 ml N_2 (16°, 742 mm). 0.0336 g sub.: 1.480 ml N_2 (16°, 742 mm). 0.0238 g sub.: 29.60 ml 0.0505 N $Na_2S_2O_3$. 0.0214 g sub.: 27.2 ml 0.0505 N $Na_2S_2O_3$. 0.1532 g sub.: 21.65 g dioxane: Δt 0.130° 0.1202 g substance: 22.32 g dioxane: Δt 0.104°. Found %: N 5.10, 5.08; OCH_3 32.47, 33.19. M 252.0, 239.8. $C_9H_{14}O_5NSP$. Calculated %: N 5.02; OCH_3 33.34. M 279.25.

Trimethyl o-tolylsulfonimidophosphate. Yield 2.23 g (76.0%). Crystallizes from 50% ethanol or from carbon tetrachloride as well-formed prisms, m.p. 74-75°.

0.0248 g sub.: 1.052 ml N_2 (20°, 740 mm). 0.0262 g sub.: 1.120 ml N_2 (20°, 740 mm). 0.0201 g sub.: 24.05 ml 0.0505 N $Na_2S_2O_3$. 0.0234 g sub.: 28.20 ml 0.0505 N $Na_2S_2O_3$. Found %: N 4.81, 4.85; OCH_3 31.23, 31.46. $C_{10}H_{16}O_5NSP$. Calculated %: N 4.77; OCH_3 31.73.

Trimethyl p-tolylsulfonimidophosphate. Yield 2.36 g (80.5%). Stout, transparent, regularly formed prisms (from ether), m.p. 44-45°.

0.0272 g sub.: 32.30 ml 0.0505 N $Na_2S_2O_3$. 0.0227 g sub.: 26.90 ml 0.0505 N $Na_2S_2O_3$. Found %: OCH_3 31.00, 30.94. $C_{10}H_{18}O_5NSP$. Calculated %: OCH_3 31.73.

Trimethyl α-naphthylsulfonimidophosphate. Yield 2.36 g (71.7 %). Colorless, regularly formed prisms (from alcohol or carbon tetrachloride), m.p. 84 -85°.

0.0302 g sub.: 1.080 ml N_2 (14°, 752 mm). 0.0284 g sub.: 1.020 ml N_2 (14°, 752 mm). 0.0322 g sub.: 35.0 ml 0.0505 N $Na_2S_2O_3$. 0.0293 g substance: 31.6 ml 0.0505 N $Na_2S_2O_3$. Found %: N 4.21, 4.23; OCH_3 28.38, 28.16. $C_{13}H_{16}O_5NSP$. Calculated %: N 4.25; OCH_3 28.27.

Trimethyl β-naphthylsulfonimidophosphate. Yield 2.62 g (79.6 %). Crystallizes nicely from carbon tetrachloride in the form of slender, lustrous scales, m.p. 93-94°

0.0294 g substance: 1.068 ml N_2 (16°, 748 mm). 0.0301 g substance: 32.4 ml 0.0505 N $Na_2S_2O_3$. Found %: N 4.22; OCH_3 28.10. $C_{13}H_{16}O_5NSP$. Calculated %: N 4.25; OCH_3 28.27.

Dimethylphenylsulfonamidophosphate. Yield 0.4 g (15.1%). Small, transparent cubes (water), m.p. 108-109°.

0.0260 g substance: 23.35 ml 0.0505 N $Na_2S_2O_3$. 0.4062 g substance: 7.95 ml 0.2046 N NaOH. 0.1055 g substance: 11.28 ml CH_4 (16°, 750 mm). Found %: OCH_3 23.45. Equiv.• 1.06; active H atoms (Terentyev) 1.16. $C_8H_{12}O_5NSP$. Calculated OCH_3 23.41; equiv. 1.00; active H atoms 1.00.

Dimethyl o-tolylsulfonamidophosphate. Yield 0.57 g (20.4%) Stout clusters of prisms (50% alcohol) m.p. 145-146°.

0.0304 g substance: 25.4 ml 0.0505 N $Na_2S_2O_3$. 0.3866 g substance: 6.90 ml 0.2046 N NaOH. 0.0988 g substance: 9.33 ml CH_4 (15°, 749 mm). Found %: OCH_3 21.81. Equiv. 1.02; active H atoms 1.08. $C_9H_{14}O_5NSP$. Calculated %: OCH_3 22.22. Equiv 1.00; active H atoms 1.00.

Dimethyl p-tolylsulfonamidophosphate. Yield 0.25 g (8.95%). Crystallizes nicely from water or dilute ethanol in the form of stout colorless prisms, m.p. 110-111°.

0.0216 g substance: 18.20 ml 0.0505 N $Na_2S_2O_3$. 0.2556 g substance: 4.52 ml 0.2046 N NaOH. Found %: OCH_3 20.00. Equiv. 1.01. $C_9H_{14}O_5NSP$. Calculated %: OCH_3 22.22. Equiv. 1.00.

Dimethyl α- naphthylsulfonamidophosphate. Yield 0.78 g (25%). Crystallizes nicely from ethyl acetate or dilute (50%) alcohol in the form of prisms, m.p. 164-165°.

0.0293 g substance: 1.114 ml N_2 (17°, 752 mm). 0.0202 g substance: 15.10 ml 0.0505 N $Na_2S_2O_3$. 0.3062 g substance: 4.78 ml 0.2046 N NaOH. Found %: N 4.43; OCH_3 19.52. Equiv. 1.01. $C_{12}H_{14}O_5NSP$. Calculated %: N

Dimethyl-β-naphthylsulfonamidophosphare. Yield 0.4 g (12.3%). Crystallizes from water of dilute (50%) alcohol in the form of long, lustrous needles, m.p. 144-145°.

0.0311 g substance: 22.65 ml 0.0505 N $Na_2S_2O_3$. 0.1864 g substance: 3.05 ml 0.2046 N NaOH. Found %: OCH_3 19.01. Equiv. 1.06. $C_{12}H_{14}O_5NSP$. Calculated %: OCH_3 19.69. Equiv. 1.00.

Reaction of Trichlorophosphazosulfonaryls with a Solution of Sodium Ethoxide in Ethanol

The reaction of trichlorophosphazosulfonaryls with a solution of sodium ethoxide was performed by the same procedure as for the reaction with sodium methoxide. The only difference was that the sodium chloride formed in the reaction comes down in a very finely dispersed state and its removal by filtration is extremely difficult, because it either passes through the filter or rapidly clogs it and brings filtration to a standstill. Without separating off the sodium chloride, the reaction mixture is concentrated by driving off the benzene and alcohol in vacuum on a boiling water bath. To the semiliquid mass remaining after elimination of the solvents is added 30 ml water with good stirring. The water-insoluble triethyl esters separate as a heavy, oily layer.

In the case of the triethyl esters of α- and β-naphthylsulfonimidophosphoric acids, the oily layer fairly readily and quickly crystallizes when rubbed with a glass rod. The crystalline portion is drained, washed with water and crystallized.

The triethyl esters of phenyl-, o- and p-tolylsulfonimidophosphoric acids do not crystallize from an aqueous mixture, and therefore they are separated by extracting the aqueous mixture with benzene. The benzene extract is washed with water and dried with sodium sulfate before the benzene is driven off on the water bath to leave a light-yellow, oily liquid. In the case of triethyl o-tolylsulfonimidophosphate this liquid readily crystallizes on cooling with iced water. The triethyl esters of phenyl-and p-tolylsulfonimidophosphoric acids are liquids which do not solidify when cooled with a mixture of snow and salt.

• Here and subsequently using phenolphthalein as indicator.

By this method were prepared the following esters.

Triethyl phenylsulfonimidophosphate. Yield 2.62 g (81.5%). Liquid.

0.0379 g sub.: 38.53 ml 0.05133 N $Na_2S_2O_3$. 0.0266 g sub.: 28.00 ml 0.05133 N $Na_2S_2O_3$. Found %: OC_2H_5 39.17, 40.56 $C_{12}H_{20}O_5NSP$. Calculated %: OC_2H_5 42.08.

Triethyl o-tolylsulfonimidophosphate. Yield 2.75 g (82.1%). Crystallizes from a slowly evaporating ethereal solution in the form of stout, transparent prisms, length 1.5-2 cm, m.p. 35-37°.

0.0341 g sub.: 1.213 ml N_2 (21°, 756 mm). 0.0281 g sub.: 29.65 ml 0.0505 N $Na_2S_2O_3$. Found %: N 4.11; OC_2H_5 39.98. $C_{13}H_{22}O_5NSP$. Calculated %: N 4.18; OC_2H_5 40.32.

Triethyl p-tolylsulfonimidophosphate. Yield 2.64 g (78.7%). Liquid.

0.0333 g sub.: 33.90 ml 0.0505 N $Na_2S_2O_3$. 0.0289 g sub.: 29.43 ml 0.0505 N $Na_2S_2O_3$. Found %: OC_2H_5 38.58, 38.58. $C_{13}H_{22}O_5NSP$. Calculated %: OC_2H_5 40.32.

Triethyl α-naphthylsulfonimidophosphate. Yield 3.21 g (86.4%). Separates from ethanol in the form of regular prisms, m.p. 94-95°.

0.0382 g sub.: 1.292 ml N_2 (20°, 742 mm). 0.0248 g sub.: 23.80 ml 0.0505 N $Na_2S_2O_3$. 0.2106 g sub.; 22.61 g dioxane: Δt 0.126°. Found %: N 3.85; OC_2H_5 36.37. M 342.2. $C_{16}H_{22}O_5NSP$. Calculated %: N 3.77; OC_2H_5 36.39. M 371.38.

Triethyl β-naphthylsulfonimidophosphate. Yield 2.80 g (75.4%). Separates from a slowly evaporating ethereal solution in the form of stout prisms, m.p. 51-52°.

0.0292 g sub.: 0.930 ml N_2 (17°, 748 mm). 0.0236 g sub.: 22.55 ml 0.0505 N $Na_2S_2O_3$. Found %: N 3.63; OC_2H_5 36.22. $C_{16}H_{22}O_5NSP$. Calculated %: N 3.77; OC_2H_5 36.39.

Diethyl phenylsulfonamidophosphate. Yield 0.20 g (6.82%). Readily soluble in hot water. Crystallizes nicely from dilute (50%) ethanol as stout prisms, m.p. 111-112°.

0.0272 g sub.: 21.70 ml 0.0505 N $Na_2S_2O_3$. 0.1003 g sub.: 1.68 ml 0.2046 N NaOH. Found %: OC_2H_5 30.23. Equiv. 1.005. $C_{10}H_{16}O_5NSP$. Calculated %: OC_2H_5 30.73. Equiv. 1.00

Diethyl o-tolylsulfonamidophosphate. Yield 0.3 g (9.76%). Prisms (from 50% alcohol). m.p. 97-98°.

0.0337 g sub.: 26.1 ml 0.0505 N $Na_2S_2O_3$. 0.1545 g sub.: 2.47 ml 0.2046 N NaOH. Found %: OC_2H_5 29.35. Equiv. 1.005. $C_{11}H_{18}O_5NSP$. Calculated %: OC_2H_5 29.33. Equiv. 1.00.

Diethyl p-tolylsulfonamidophosphate. Yield 0.23 g (7.48%). Fine, regularly formed prisms (from water), m.p. 105-106°.

0.0207 g sub.: 15.85 ml 0.0505 N $Na_2S_2O_3$. 0.1232 g sub.: 1.97 ml 0.2046 N NaOH. Found %: OC_2H_5 29.02. Equiv. 1.005. $C_{11}H_{18}O_5NSP$. Calculated %: OC_2H_5 29.33. Equiv. 1.00.

Diethyl α-naphthylsulfonamidophosphate. Yield 0.28 g (8.16%). Best purified by reprecipitation from alkali solution followed by crystallization from ethanol. Stout, regularly formed prisms, m.p. 154-155°.

0.0193 g sub.: 13.35 ml 0.0505 N $Na_2S_2O_3$. 0.4591 g sub.: 6.65 ml 0.2000 N NaOH. 0.1187 g sub.: 9.45 ml CH_4 (16°, 749 mm). Found %: OC_2H_5 26.21. Equiv. 0.994; active hydrogen atoms 1.11. $C_{14}H_{18}O_5NSP$. Calculated %: OC_2H_5 26.25. Equiv. 1.00; active hydrogen atoms 1.00.

Diethyl β-naphthylsulfonamidophosphate. Yield 0.7 g (20.4 %). On crystallization from dilute ethanol (30-40%) it separates as regular, small prisms, m.p. 161-162°.

0.0164 g sub.: 11.30 ml 0.0505 N $Na_2S_2O_3$. 0.1860 g sub.: 2.70 ml 0.2000 N NaOH. Found %: OC_2H_5 26.12. Equiv. 0.997. $C_{14}H_{18}O_5NSP$. Calculated %: OC_2H_5 26.25. Equiv. 1.00.

Reaction of Trichlorophosphazosulfonaryls with a Solution of Sodium n-Butoxide in n-Butyl Alcohol

In a three-necked, 150 ml flask, equipped with reflux condenser, thermometer and dropping funnel, is dissolved 0.7 g (0.031 mole) metallic sodium in 20 ml anhydrous butyl alcohol with heating to 120°. After the whole of the sodium has dissolved, the reflux condenser is replaced by a stirrer.

Then the contents of the flask are cooled to 10° and with energetic stirring a solution of 0.01 mole trichlorophosphazosulfonaryl in 30 ml dry benzene is run in at such a rate that the temperature of the reaction mixture does not rise above 20°. The reaction mixture is heated at 50° for 30 minutes. For separation of the tributyl esters the mixture is evaporated by careful heating in vacuum on a boiling water bath to drive off the benzene and alcohol. Into the viscous, opalescent liquid residue is run 30 ml water and the mixture is well shaken; it is then extracted with 50 ml ether. The ethereal extract is filtered and dried with sodium sulfate; the solvent is then driven off in vacuum on a water bath, leaving a residue of tributyl ester as a liquid which does not crystallize on cooling to -21°. All these esters possess a faint characteristic odor and have a faint yellow color.

Tri-n-butyl phenylsulfonimidophosphate. Yield 3.45 g (85.1%). Liquid.

0.0311 g sub.: 0.885 ml N_2 (18°, 752 mm). 0.0307 g sub.: 0.852 ml N_2 (18°, 752 mm). Found %: N 3.30, 3.22. $C_{18}H_{32}O_5NSP$. Calculated %: N 3.45.

Tri-n-butyl o-tolylsulfonimidophosphate. Yield 3.72 g (88.7%). Liquid.

d_4^{20} 1.111; n_D^{20} 1.491.

0.0470 g sub.: 1.272 ml N_2 (18°, 752 mm). 0.0409 g sub.: 1.100 ml N_2 (18°, 752 mm). Found %: N 3.14, 3.12. $C_{19}H_{34}O_5NSP$. Calculated %: N 3.34.

Tri-n-butyl α-naphthylsulfonimidophosphate. Yield 3.96 g (86.9%). Viscous liquid.

d_4^{20} 1.141; n_D^{20} 1.530.

0.0468 g sub.: 1.280 ml N_2 (20°, 751 mm). 0.0423 g sub.: 1.050 ml N_2 (20°, 751 mm). Found %: N 3.05, 2.86. $C_{22}H_{34}O_5NSP$. Calculated %: N 3.08.

Tri-n-butyl β-naphthylsulfonimidophosphate. Yield 4.14 g (90.9%). Viscous liquid.

d_4^{20} 1.135; n_D^{20} 1.532.

0.0454 g sub.: 1.180 ml N_2 (20°, 751 mm). Found %: N 2.99. $C_{22}H_{34}O_5NSP$. Calculated %: N 3.08.

Hydrolysis of Full Esters of Arylsulfonimidophosphoric Acids with Alcoholic Hydrochloric Acid

Into a 50 ml flask, fitted with reflux condenser, is introduced 0.001 mole trialkyl ester of arylsulfonimidophosphoric acid and 25 ml 0.2 N alcoholic solution of hydrochloric acid (5.0 ml 1 N aqueous hydrochloric acid and 20 ml alcohol); the mixture is heated to the boil for an hour and the alcohol is driven off from the reaction mixture in the vacuum of a water pump. The residue is neutralized with N NaOH solution until neutral to phenolphthalein, and then the non-hydrolyzed full ester is extracted with 20 ml ethyl ether. The ethereal extract is dried with sodium sulfate and filtered; the solvent is removed in vacuum on a water bath. The aqueous solution after separation of non-hydrolyzed ester is evaporated in vacuum to a volume of about 5 ml and acidified with a few drops of concentrated hydrochloric acid until acid to Congo. The dialkyl esters, which separate from the acidified solution in the form of an oil, readily crystallize when rubbed with a glass rod. The crystalline precipitate is drained and dried. Yields of the hydrolysis products are set forth in Table 2.

The products of hydrolysis were identified from the melting point and titration data. Within the limits of experimental error the melting points and the titration values corresponded to those of the pure substances.

Hydrolysis of Full Esters of Arylsulfonimidophosphoric Acids with an Alcoholic Solution of Sodium Hydroxide

To 0.001 mole full ester of the arylsulfonimidophosphoric acid were added 5 ml of N NaOH solution and 20 ml ethyl alcohol. The mixture was heated to the boil for an hour, after which the alcohol was driven off in vacuum. The residue was a transparent solution and consequently did not contain the full ester. After acidification of the solution with a little conc. hydrochloric acid, the dialkyl ester comes out in the form of a viscous, heavy oil which readily crystallizes on rubbing with a glass rod. The crystalline precipitate is drained, washed several times with water, dried and crystallized. The so-prepared dialkyl esters of arylsulfonamidophosphoric acids have sharp melting points after crystallization, and mixed samples with the corresponding diesters prepared by other methods do not show a depression of melting point. For yields and melting points see Table 3.

Properties and analyses of the dimethyl and diethyl esters have been detailed above.

Di-n-butyl α-naphthylsulfonamidophosphate is a colorless crystalline substance with a remarkably bitter taste. The ester has good solubility in alcohol, acetone and carbon tetrachloride; it is insoluble in water and cold ligroin. It crystallizes from ligroin in the form of fine prisms, m.p. 75-77°.

0.0364 g sub.: 0.0723 ml CO_2; 0.0219 g H_2O. 0.5026 g sub.: 6.20 ml 0.2046 N NaOH. Found %: C 54.16; H 6.73. Equiv. 1.01. $C_{18}H_{26}O_5NSP$. Calculated %: C 54.14; H 6.56. Equiv. 1.00.

Preparation of Dialkyl Esters of Arylsulfonamidophosphoric Acids directly from the Trichlorophosphazosulfonaryls

In a round-bottomed flask, fitted with a reflux condenser and dropping funnel, is placed 30 ml anhydrous methyl or ethyl alcohol, and 1.04 g (0.045 g-atom) metallic sodium is added. When the sodium has dissolved, the reflux condenser is replaced by a stirrer, and 0.01 mole trichloriphosphazosulfonaryl in 30 ml dry benzene is run in with energetic stirring. During this stage the reaction temperature rises to 40-50°. At the end of the reaction the benzene and alcohol are distilled off in vacuum on a water bath. The dry residue is dissolved in 20 ml water and acidified with hydrochloric acid until acid to congo. The dialkyl ester separates in the form of a heavy oil which readily crystallizes when rubbed with a glass rod. The crystalline product is drained, washed several times with small portions of water, dried and crystallized.

For yields of reaction products see Table 4.

The dialkyl esters were identified by their melting points and titration values. Mixed tests with the corresponding dialkyl esters prepared by other methods (see above) did not give a metling point depression.

Preparation and Properties of α- and β-Trichlorophosphazosulfonnaphthyls

Into a round-bottomed flask were introduced 0.150 mole (31.03 g) finely pulverized and thoroughly dried α-naphthalenesulfamide, 0.152 mole (31.7 g) pure phosphorus pentachloride and 35 ml dry carbon tetrachloride. The flask was closed with a reflux condenser whose upper end was connected to a hydrogen chloride absorbent. The mixture was heated on a boiling water bath.

After the solvent had begun to boil, a fairly vigorous evolution of hydrogen chloride started. The reaction mixture gradually became fluid and after 20 minutes it had become completely liquid. Hydrogen chloride evolution ceased after an hour and the reaction came to an end. The flask then contained an amber-colored liquid.

Heating was stopped after the reaction came to an end; 45 ml hot carbon tetrachloride was run in, the upper end of the condenser was closed with a calcium chloride tube and the mixture was left to crystallize. The separated crystalline mass was drained, washed with carbon tetrachloride and dried in vacuum at 80-90°. Yield 48.1 g (93.5%).

α-Trichlorophosphazosulfonnaphthyl does not possess a sharp melting point. At 107-110° it becomes "moist", and at 110-112° it melts to a turbid liquid which finally clarifies at 117°. Subsequent repeated crystallization from carbon tetrachloride or ligroin does not change the melting point.

0.1664 g sub.: 9.52 ml 0.05 N H_2SO_4. 0.1390 g sub.: 8.01 ml 0.05 N H_2SO_4. 1.2928 g sub.: 185.8 ml 0.0989 N NaOH. 0.3822 g sub.: 26.6 ml 0.2046 N NaOH. 0.5545 g substance: 13.23 g benzene: Δt 0.616°. 0.4155 g substance: 13.68 g benzene: Δt 0.444°. Found %: N 4.01, 4.03. Equiv. 4.94, 4.95; M 345, 349. $C_{10}H_7O_2NSPCl_3$. Calculated %: N 4.09. Equiv. 5.00; M 342.5.

β-Trichlorophosphazosulfonnaphthyl is prepared in the same way as the α-compound but the reaction takes place much more slowly (3 to 3.5 hours). It must also be noted that when preparing the β-trichlorophosphazosulfonnaphthyl the heating of the reaction mixture should not be interrupted during the course of the whole reaction. Cooling rapidly results in crystallization of the difficultly soluble β-trichlorophosphazosulfonnaphthyl which envelops the unreacted β-naphthalenesulfamide. On the renewal of the heating, the separated β-trichlorophosphazosulfonnaphthyl does not completely go back into solution and a considerable amount of the β-naphthalenesulfamide remains unreacted.

At the end of the reaction, 50 ml carbon tetrachloride is run in and the mixture is left to crystallize. The crystalline product is washed with carbon tetrachloride and dried in a vacuum on a boiling water bath.

β-Trichlorophosphazosulfonnaphthyl is obtained in the form of a snow-white, crystalline powder melting at 130-132°. Yield 46.3 g (90.1%).

The β-naphthalenesulfamide used in the reaction must be thoroughly ground to a fine powder and well dried. The phosphorus pentachloride does not need to be pulverized since it dissolves readily in hot carbon tetrachloride.

0.1268 g sub.: 7.40 ml 0.05 N H_2SO_4. 0.1784 g sub.: 10.32 ml 0.05 N H_2SO_4. 1.2216 g sub.: 175.8 ml 0.0989 N NaOH. 1.0960 g sub.: 76.1 ml 0.2046 N NaOH. Found %: N 4.09, 4.05. Equiv. 4.946, 4.937. $C_{10}H_7SO_2NPCl_3$. Calculated %: N 4.09. Equiv. 5.00.

α- and β-trichlorophosphazosulfonnaphthyls are colorless and odorless crystalline substances. They are readily soluble in acetone, chloroform, ethyl acetate, benzene and hot carbon tetrachloride; they are sparingly soluble in ether and ligroin.

β-Trichlorophosphazosulfonnaphthyl is less soluble in nearly all solvents than the α-compound. Thus, 100 ml carbon tetrachloride at 19° dissolves 2.25 g α-trichlorophosphazosulfonnaphthyl; in the same conditions 1.39 g β-compound dissolves. In boiling carbon tetrachloride α-trichlorophosphazosulfonnaphthyl dissolves very easily (over 200 g in 100 ml solvent), whereas only about 20 g β-compound dissolves in the same amount of solvent. 100 ml benzene at 19° dissolves 5.7 g β-trichlorophosphazosulfonnaphthyl and more than 20 g of the α-compound. Both compounds are readily soluble in boiling benzene.

The trichlorophosphazosulfonnaphthyls react slowly with cold water, finally forming the corresponding naphthalenesulfamides.

On mixing 1 g (0.003 mole) α- or β-trichlorophosphazosulfonnaphthyl with 50 ml water and leaving the mixture to stand at room temperature, a nearly quantitative yield of the corresponding naphthalenesulfamide is obtained after 3 days. In an alkaline medium, in presence of NaOH, hydrolysis takes place with formation of salts of naphthalenesulfonamidophosphoric acids, α- and β-$C_{10}H_7SO_2NHPO(ONa)_2$. The free acids are readily hydrolyzed. Their sodium salts, however, are extremely stable and do not hydrolyze after prolonged boiling with water.

In an alkaline medium α-trichlorophosphazosulfonnaphthyl hydrolyzes twice as quickly as the β-compound; one of the three chlorine atoms enters with particular facility into reaction with water, alcohol, and ammonia.

If 0.34 g (0.001 mole) α- or β-trichlorophosphazosulfonnaphthyl is added to 50 ml 0.04 N NaOH solution (0.002 mole) at 20°, then energetic stirring causes the alkaline reaction (to phenolphthalein) to disappear in 15 minutes in the case of the α-compound and in 32 minutes in that of the β-compound, and the greater part of the substance goes into solution. If double the amount of NaOH is taken (0.004 mole, 50 ml 0.08 N solution), the color of the indicator disappears in the case of the α-compound in 1 and three-quarter hours and in that of the β compound in 3 and three-quarter hours.

Consequently the first stage of hydrolysis

$$C_{10}H_7SO_2N{=}PCl_3 + H_2O \rightarrow C_{10}H_7SO_2NHPOCl_2 + HCl$$

both for the α- and the β-trichlorophosphazosulfonnaphthyl is seven times as rapid as the second stage in spite of the fact that the first stage takes place in heterogeneous conditions and the second in solution.

On boiling with water the trichlorophosphazosulfonnaphthyls are quickly and completely hydrolyzed with formation of naphthalenesulfamide, hydrogen chloride and phosphoric acid. Neutralization of the acidic products of hydrolysis of trichlorophosphazosulfonnaphthyls with a standard solution of NaOH is a rapid and convenient method of analysis of trichlorophosphazosulfonnaphthyls.

When kept in sealed ampoules or in flasks with a good ground-glass stopper, the trichlorophosphazosulfonnaphthyls can be stored unchanged for an indefinitely long period. When stored in the air or in poorly stoppered flasks, they slowly change and evolve hydrogen chloride due to reaction with moist air.

Like the benzene derivatives, the trichlorophosphazosulfonnaphthyls react energetically with ammonia, amines and alcohols. With phenol the reaction only takes place when heat is applied.

α- and β-trichlorophosphazosulfonnaphthyls decompose completely when heated at atmospheric pressure or in vacuum (down to 0.5 mm) and do not distil. They can be purified by recrystallization from carbon tetrachloride or ligroin. Usually, however, this is unnecessary because perfectly pure substances are obtained when using perfectly pure and dry sulfamide and phosphorus pentachloride, and the products are suitable for any preparative purposes.

SUMMARY

1. A study was made of the reaction between trichlorophosphazosulfonaryls and sodium methoxide, ethoxide and butoxide.

2. A number of new methyl, ethyl and butyl esters of arylsulfonimidophosphoric acids were prepared and their properties described.

3. The products of acidic and alkaline hydrolysis of the full esters of arylsulfonimidophosphoric acids were studied.

4. A series of dialkyl esters of arylsulfonamidophosphoric acids were prepared and their properties described.

5. A method was developed for direct preparation of dialkyl esters of arylsulfonamidophosphoric acids from alkoxides and trichlorophosphazosulfonaryls.

6. The synthesis and properties of α- and β-trichlorophosphazosulfonnaphthyls are described.

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* See Consultants Bureau Translation, p. 329.

SYNTHESIS OF SOME N-OXIDES OF PHENAZINE DERIVATIVES

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The pigment iodinin isolated from Chromobacterium iodinum is 1,5-dihydroxyphenazine-N, N'-dioxide (I) [1]*. This pigment exerts bacteriostatic action on various forms of bacteria [2] in a similar manner to other natural phenazine pigments - pyocyanine (II) and chlororaphine (III) [3].

This greatly stimulated interest in the chemistry of phenazine compounds, particularly the hydroxy derivatives and the N-oxides of phenazine. Here we must refer readers to publications in recent years by A.I. Kiprianov, and his co-workers, S.B. Serebryany, V.P. Chernetsky and others, who have greatly enriched our knowledge in the field of the chemistry of phenazine and its derivatives [1, 5-11].

Continuing our studies in the field of phenazine derivatives [4, 12-14], we were interested in the N-oxides of phenazines and in particular in the N-oxides of phenazine-1-carboxylic acid. This acid is the foundation of the molecule of the pigment chlororaphine (III) which is an unusual quinhydrone of the amide of this acid ("hydroxychlororaphine") and its dihydro derivative [4].

On oxidizing phenazine-1-carboxylic acid as well as its amide with hydrogen peroxide in glacial acetic acid, we obtained substances with a bright-orange color whose analysis for nitrogen and whose polarograms identified them as N-monoxides. We may point out that in these conditions of oxidation, phenazine readily gives the N,N'-dioxide (IV), i.e. an oxygen atom here adds on to each nitrogen atom.

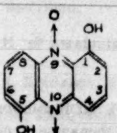
The difficulty of addition of a second oxygen in the case of oxidation of phenazine-1-carboxylic acid and its amide is apparently due to the steric hindrance resulting from the presence of a carboxyl and carboxamido group in the 1-position. It must therefore be postulated that an oxygen atom adds on to the nitrogen remote from the COOH- and $CONH_2$- groups (V, VI).

Similar cases of steric hindrance in the preparation of phenazine N-oxides have also been observed in the past. Thus, 1,2-benzophenazine gives a monoxide of structure (VII) [15]. (Compare also the preparation of monoxides in the oxidation of 1-ethoxyphenazine [10] and 1,5-dichlorophenazine [16]).

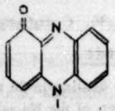
The prepared N-oxides are well-crystallizable substances. Phenazine carboxylic acid N-oxide gives a sodium salt which is readily soluble in water and is probably the first stable, water-soluble derivative of phenazine N-oxide.

Notwithstanding that the N-oxide of the amide with the structure (VI) contains the skeleton of the antibiotics iodinin (I) and chlororaphine (III), its bacteriostatic action proved to be insignificant and similar to the action of phenazine-1-carboxylic acid and its amide [17,18, 19].

In addition to the synthesis of the above oxides (V and VI) which are related to chlororaphine, we effected the synthesis of 2,6-dihydroxyphenazine-N,N'-dioxide (XI), an isomer of iodinin (I). Since, however, Vivian's paper [20] on the synthesis of the compound has appeared, we limit ourselves here to a description of a new method of preparation of 2,6-dichlorophenazine (VIII) which we used as an intermediate for the synthesis of the ethoxy derivative (X) and isoiodinin (XI).



(I)



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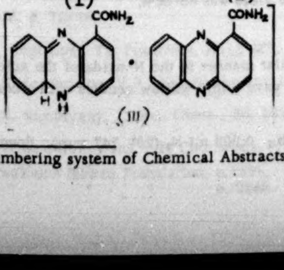

(III)

2,6-Dichlorophenazine (VIII) was obtained by the action of phosphorus oxychloride on phenazine-N,N'-dioxide (IV). Formation of a chloro derivative by the action of $POCl_3$ on an N-oxide is known, for example, in the case of the N-oxide of quinoline and pyridine [21]; in the case of phenazine N-oxides, this reaction is here applied for the first time (see Experimental). Product (VIII) was identified as the dichloro derivative obtained by Bamberger [22].

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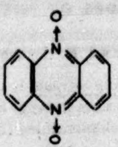
* On the numbering system of Chemical Abstracts iodinin is 1,6-dihydroxyphenazine-5,10-dioxide.- Publisher.



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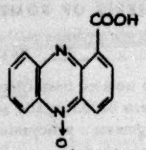

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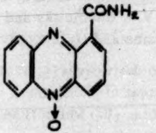

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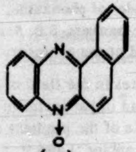

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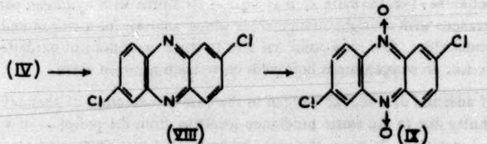
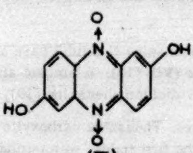
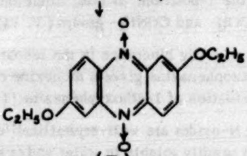




(XI)



(X)

EXPERIMENTAL

1) Phenazine-1-Carboxylic Acid N-oxide

To a solution of 0.5 g phenazine-1-carboxylic acid in 25 ml glacial acetic acid was added 2.5 ml perhydrol (30%); a part of the phenazine-1-carboxylic acid then came down in the form of a fine precipitate. The reaction mass was heated on a water bath at 50-55°. The green precipitate of phenazine-1-carboxylic acid gradually went into solution, and after 1 and one-half to 2 hours a crystalline, bright-yellow precipitate of oxidation product came down. After 10-12 hours' standing at room temperature, the precipitate was filtered, washed with water and dried at 50°. Yield 56%; m.p. 218-219°. Recrystallization from glacial acetic acid yielded fine, bright-yellow needles with a constant m.p. of 223-224°.

4.430 mg sub.: 0.460 ml N_2 (19°, 738 mm). Found %: N 11.80. $C_{13}H_8O_3N_2$. Calculated %: N 11.68.

2) Na Salt of Phenazine-1-Carboxylic Acid N-oxide

0.5 g phenazine-1-carboxylic acid N-oxide was dissolved by heating in 20 ml 2% NaOH solution. The dark solution was filtered hot. On cooling, beautiful yellow platelets of the Na salt of phenazine-1-carboxylic acid N-oxide came down. After recrystallization from water the yield was 55-56%.

3) Phenazine-1-Carboxamide N-oxide

Phenazine-1-carboxamide N-oxide was obtained in a similar manner to the N-oxide of the acid. Yield 47%; m.p. 241-242°. Recrystallization from glacial acetic acid gave bright-yellow needles with a constant m.p. of 249-250°.

4.090 mg sub.: 0.627 ml N_2 (22°, 747 mm). 3.790 mg sub.; 0.568 ml N_2 (20°, 747 mm). Found %: N 17.44, 17.18. $C_{13}H_9O_2N_3$. Calculated %: N 17.57.

4) Action of $POCl_3$ on Phenazine-N,N'-dioxide

2 g N,N'-dioxide was heated at the boil with 40 ml phosphorus oxychloride. At the start the yellow solution gradually darkened to brown.

After 3 hours heating the reaction solution was poured onto ice. The resultant light-brown precipitate was filtered off, washed with water, and then purified by dissolving in conc. HCl. The hydrochloric acid solution was filtered and the product was precipitated by adding ammonia until the reaction was alkaline. The greenish-yellow precipitate was filtered off, washed with water, and dried at 100°. Weight 1.9 g.

The precipitate comprised a mixture of chloro derivatives of phenazine and had the unsharp m.p. of 110-116°.

The mixture was resolved by taking advantage of the differing solubilities of the chloro derivatives in ethanol.

Treatment of the mixture at the boil with 50 ml ethanol caused a part of the precipitate to go into solution. The insoluble portion was filtered off, dried, and crystallized from a mixture of glacial acetic acid and xylene (1:1). Yellow needles separated out with m.p. 264-265°, identical with the melting point of 2,6-dichlorophenazine (0.05 g).

A mixed sample with the 2,6-dichlorophenol prepared by Bamberger's method [22] melted without depression.

3.110 mg sub.: 0.311 ml N_2 (20°, 751 mm). Found %: N 11.53. $C_{12}H_6N_2Cl_2$. Calculated %: N 11.25.

From the mother liquor after distillation of the ethanol and four recrystallizations of the residual product from ethanol was isolated a substance with m.p. 175°. Weight 0.08 g. This proved identical with 2-chlorophenazine-N-oxide prepared by condensation of p-nitrochlorobenzene with aniline in presence of KOH.

4.840 mg sub.: 0.519 ml N_2 (24°, 734 mm). Found%: N 11.90. $C_{12}H_7ON_2Cl$. Calculated %: N 12.15.

Action of $POCl_3$ on Phenazine-N-oxide

2 g phenazine-N-oxide was heated for 3 hours with 40 ml $POCl_3$ at the boil. The phenazine-N-oxide dissolved nicely in the $POCl_3$ to a light-yellow solution which darkened on heating. After 3 hours heating the solution was poured onto ice, when a yellow precipitate came down with m.p. 108-110°. Weight 1.6 g.

Recrystallization from ethanol gave yellow needles of 2-chlorophenazine with m.p. 138° (literature data: 138°) [23]. Weight 0.3 g.

A mixed test with 2-chlorophenazine obtained by condensation of p-chloroaniline with nitrobenzene by Wohl's method did not give a melting point depression.

SUMMARY

1. It is shown that oxidation of phenazine-1-carboxylic acid and its amide with hydrogen peroxide leads to the monoxides (V and VI). Apparently the presence of the carboxyl or the carboxamido group in the 1-position hinders the addition of a second oxygen atom to the nitrogen atom (in the 9-position).

2. A new example of formation of chloro derivatives of phenazine by the action of $POCl_3$ on phenazine N-oxides is described.

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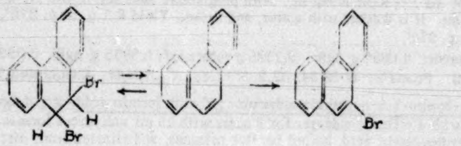
IMIDAZOLE DERIVATIVES

XIII. BROMINATION OF 1,2-NAPHTHIMIDAZOLE [1]

L. S. Efros, L. N. Kononova, and Ya. Eded

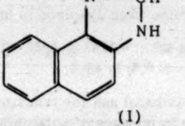
In the preceding communication[1] it was shown that in accord with our theoretical considerations on the character of the influence of the imidazole ring on disturbance of equivalence of bonds in molecules containing condensed rings, 1,2-naphthimidazole (I) behaves like phenanthrene on oxidation.

Extremely characteristic of phenanthrene is also the reaction with bromine which, in addition to smooth formation of the substitution product (the 9-bromo derivative), leads to addition of a bromine molecule at the 9,10- unsaturated bond with formation of a labile product which for a long time was erroneously regarded as an intermediate product of bromination[2]:



It therefore appeared of interest to study the bromination of 1,2-naphthimidazole (I) and thereby continue the comparison of this substance with phenanthrene.

It was found that bromination of 1,2-naphthimidazole proceeds in mineral acid aqueous solutions, in solvents like methyl alcohol and glacial acetic acid, and (most quickly) in an aqueous alkaline medium. In all the product of bromination that we isolated was a monobromo derivative – 4-bromonaphthimidazole (II)[*]:



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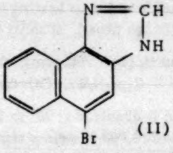

(II)

The structure of the bromination product was confirmed by its synthesis from 4-bromo-1,2-naphthylalendiamine, as described under Experimental. For the second part of the research – study of the addition of bromine to 1,2-naphthimidazole – we decided, as in the case of phenanthrene, to conduct this reaction in glacial acetic acid in which the substitution reaction, as we established, proceeds fairly slowly. Actually when the reaction is carried out in sufficiently concentrated solutions, the addition of bromine is followed by separation from the solution of a faint-yellowish substance in the form of fine needles which had an odor of bromine and on heating to 100-120° evolved hydrogen bromide and became colorless. The elementary analysis revealed the presence of two bromine atoms. The compound had good solubility in methanol and ethanol and dissociated in them with loss of bromine. Titration of this free bromine showed that it amounted to 25.7 % of the total bromine content of the compound. Consequently the bromination product obtained in these conditions contained about 25% of the product of addition of bromine to 1,2-naphthimidazole and about 75% of the hydrobromide of 4-bromo-1,2-naphthimidazole (II). The latter was isolated from this product and after purification was found to be identical with the product described above.

In attempting to improve the conditions of formation of the bromine addition product, we effected the bromination in a mixture of carbon tetrachloride and glacial acetic acid at 0° and under irradiation.

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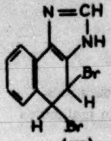
[*] The compound would be the 5-bromo derivative according to Chemical Abstracts numbering – Publisher.

Determination of the amount of bromine split off from the reaction product on dissolving in methanol showed that the product of addition of bromine to 1,2-naphthimidazole represented about 40% of the obtained substance while the product of bromination (II) was present to the extent of about 60%.

Consequently two processes take place simultaneously during the bromination of 1,2-naphthimidazole in the described conditions: formation of a substitution product (II) and formation of an addition product with the probable structure of (III).


(III)

In the light of the above data, the latter substance is much less stable than the analogous product obtained from phenanthrene. On the other hand, the substitution reaction when bromine acts upon 1,2-naphthimidazole also proceeds with considerably greater facility than the bromination of phenanthrene.

It was evidently for these reasons that we failed to select those conditions which would have enabled us to obtain the pure product of addition of bromine to the 1,2-naphthimidazole molecule. Nevertheless a definite similarity between the behavior of 1,2-naphthimidazole and phenanthrene on bromination was established by the above-described experiments.

EXPERIMENTAL

1. 4-Bromo-1,2-naphthimidazole.

a) Bromination of 1,2-naphthimidazole. 5 g 1,2-naphthimidazole is dissolved in 500 ml KOH; after 30 minutes 5 g bromine in 100 ml 1 N KOH is run in. With progressive addition of the Br, a colorless reaction product separates as fine needles. It is washed with water, and dried. Yield 8.1 g, m.p. 272°. After crystallization from dilute acetic acid, m.p. 274°.

0.1147 g substance: 0.0887 g AgBr. 0.1125 g substance; 0.0855 g AgBr. 0.0995 g substance: 9.9 ml N_2 (23°, 750 mm). Found %: Br 32.34, 32.9; N 11.32. $C_{11}H_7N_2Br$. Calculated %: Br 32.35; N 11.2.

b) Condensation of 4-bromo-1,2-naphthalenediamine [3] with formic acid. 2 g 4-bromo-1,2-naphthalenediamine is heated in a flask with a reflux condenser for 3 hours with 15 ml anhydrous formic acid. The reaction mass is diluted with 40 ml 5% hydrochloric acid, boiled for five minutes, and filtered from dirt. The filtrate is neutralized with ammonia and the reaction product collected; after several crystallizations from acetic acid, m.p. 274°; no depression in admixture with the product of bromination of 1,2-naphimidazole. Yield 1 g.

2. Product of Addition of Bromine to 1,2-Naphthimidazole

a) 1 g naphthimidazole is dissolved in a mixture of 25 ml glacial acetic acid and 25 ml carbon tetrachloride. At 20° addition is made to the solution of 0.816 g bromine in 3 ml carbon tetrachloride. Yellow crystals (needles under the microscope) rapidly settle out from the solution. They are filtered, thoroughly washed with carbon tetrachloride and dried in a vacuum-desiccator over paraffin wax.

The compound gives off bromine on heating (test with starch-iodide paper) and at 100-120° it evolves hydrobromic acid (test with congo paper). It splits off bromine when dissolved in methanol or ethanol.

0.1412 g sub.: 10.9 ml N_2 (21°, 742 mm). 0.1033 g sub.: 0.1181 g AgBr. 0.1325 g sub.: 0.1500 g AgBr. Found %: N 8.7; Br 48.6, 48.2 $C_{11}H_8N_2Br_2$. Calculated %: N 8.5; Br 48.7.

0.50 g of the substance is dissolved at 20° in 50 ml methanol and the resultant solution is titrated in a hydrochloric acid medium with 0.098 N sodium thiosulfate in presence of potassium iodide. The titration consumes 8.0 ml thiosulfate, equivalent to 25.7% of the total bromine content of the product. The same result is obtained if the substance is dissolved in methanol at 0°.

b) An experiment is performed as described in section a) but with the difference that it is run at 0° in direct sunlight. 0.5 g of the resultant product is likewise dissolved in methanol at 0° and at 20° and titrated with sodium thiosulfate. In both cases 12.1 ml thiosulfate is consumed, equivalent to 38.5% of the total bromine of the substance.

SUMMARY

1. The known similarity between 1,2-naphthimidazole and phenanthrene, previously demonstrated [1] in a study of the oxidation of 1,2-napthimidazole, is also manifested in the bromination of this compound. The latter reaction, as in the case of phenanthrene, proceeds in two directions – with formation of a 4-substituted product and of a labile and easily dissociated product of addition of a molecule of bromine to the 1,2-naphthimidazole molecule.

2. These characteristics of 1,2-naphthimidazole find their explanation by our previously expounded [4] ideas of the nature of the influence of the imidazole ring on the disturbance of the equivalence of bonds in molecules containing condensed rings.

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EMPLOYMENT OF ANTIMONY PENTACHLORIDE IN THE GUSTAVSON–FRIEDEL-CRAFTS REACTION

A.M. Petrova

The employment of antimony pentachloride in the Gustavson-Friedel-Crafts reaction has not received adequate consideration in the literature.

We carried out a number of experiments to compare $SbCl_5$ with the classic catalyst for this reaction ($AlCl_3$) as well as with $SnCl_4$.

All the experiments were performed with benzene, to which were added:

1) Halogeno derivatives in the shape of primary halogenated butanes and benzyl chloride and 2) carboxylic acid chlorides and ethyl nitrate.

Experiments with esters have been described previously [1].

Of the halogenated hydrocarbons that we tested, only benzyl chloride reacted with benzene in presence of $SbCl_5$, but the yield of diphenylmethane was lower than in the case of $AlCl_3$. The reaction did not take place with butyl chloride, bromide or iodide. It is interesting, however, that chlorination of benzene was not observed with any of these halogeno derivatives, a process which takes place readily with $SbCl_5$ alone [2]. It must be assumed that the butyl halides form a complex with $SbCl_5$ which does not react with benzene.

In our conditions benzoyl chloride with $SbCl_5$ gave a higher yield of benzophenone than with $AlCl_3$. The yield was 210% ketone calculated on the $SbCl_5$, i.e. in this case the reaction, in contrast to the synthesis with $AlCl_3$, actually possesses a catalytic character. $AlCl_3$ must be taken in equimolecular ratio to the acid chloride since in the reaction a stable complex of ketone with $AlCl_3$ is formed [3]. The complex of $SbCl_5$ with benzophenone is evidently less stable. Due to its decomposition, the $SbCl_5$ is able to convert fresh quantities of benzene and acid chloride into ketone.

On the assumption of a similar mechanism for the reaction of benzene with esters, we attempted to isolate the binary and ternary complexes in experiments with ethyl nitrate. These attempts failed completely with $AlCl_3$ and $SnCl_4$. On evaporation of solutions of $AlCl_3$ and $SnCl_4$ in excess of $C_2H_5ON_2$, decomposition takes place even at temperatures below 0°. In the former case oxides of nitrogen are evolved; in the latter case $SnCl_4$ distils off.

On adding $SbCl_5$ to ethyl nitrate there is an immediate detonation. On mixing $SbCl_5$ with ethyl nitrate in carbon tetrachloride, however, separation of a viscous, dark blue liquid is observed at a temperature of about −20°; this liquid may be assumed to be the anticipated complex. Addition of benzene to this substance gives nitrobenzene.

The yield of the latter rises if more ethyl nitrate is added.

EXPERIMENTAL

Into a three-necked flask, fitted with a mercury-sealed stirrer, a dropping funnel and a reflux condenser, is introduced 0.5 mole halogenated hydrocarbon or acid chloride and 2 moles benzene. From the dropping funnel is added 0.125 mole $SbCl_5$ with cooling and stirring. To the dropping funnel was attached a calcium chloride tube. Another calcium chloride tube was fixed to the end of the condenser and joined to a tube whose end dipped into a cylinder of water for absorption of the evolved gases. The mixture was heated at 70° for 4 hours on a water bath; the $SbCl_5$ was then decomposed with water and the hydrocarbon portion was steam distilled. The residue was extracted with ether. The benzene-ether layer was dried with calcium chloride and fractionated.

The results of the experiments are set forth in the table.

Alkylated or acylated substance	Reaction product	Yield of product on basis of catalyst used (in %)	
		$SbCl_5$	$AlCl_3$
Benzyl chloride.	Diphenylmethane	35	46.8
Benzoyl chloride.	Benzophenone	72	21.7
Acetyl chloride.	Acetophenone	0.5	0.8
Butyl bromide	sec-Butylbenzene	6	38.8
	n-Butylbenzene	0	13.1
Butyl iodide	sec-Butylbenzene	[illegible]	41.8
	n-Butylbenzene	0	9.7
Butyl chloride	sec-Butylbenzene	3	28.3
	n-Butylbenzene	0	25.4

Reaction of Ethyl Nitrate with $SbCl_5$

To a solution of 0.125 mole $SbCl_5$ in carbon tetrachloride, cooled to −21°, was added dropwise at the same temperature 0.5 mole ethyl nitrate in carbon tetrachloride. After 30 minutes a heavy, dark blue oily layer separated. After separation and washing of the lower layer with carbon tetrachloride, 2 moles of benzene was run into each layer. The wash liquor was added to the top layer. The whole was left for 3 hours and then heated for 2 hours on a water bath; it was then decomposed with water; the hydrocarbon layer was dried with $CaCl_2$ and fractionated. The upper layer contained 5.53% $C_6H_5NO_2$ and the lower layer 5.72%,reckoned on the ester.

In order to check whether the complex acts as a catalyst, repeated washings with carbon tetrachloride were followed by addition of another 0.5 mole ethyl nitrate and 2 moles benzene. Heating and working-up were conducted as described above. After fractionation the upper layer contained 3.9% $C_6H_5NO_2$ (36.6% Sb) and the lower layer 16% $C_6H_5NO_2$ (63.7% Sb).

Carbon tetrachloride slightly retards ring substitution. Thus in experiments without carbon tetrachloride, 35.5% nitrobenzene was obtained, while in carbon tetrachloride solution the yield of nitrobenzene was only 27%.

SUMMARY

1. A comparison was made of the catalytic action of $AlCl_3$ and $SbCl_5$ in reactions of benzene with some halogenated hydrocarbons, carboxylic acid halides, and ethyl nitrate. .

2. It was established that in the reaction with halogenated hydrocarbons antimony pentachloride acts much less intensively than aluminum chloride.

3. In the reaction of benzene with some acid halides, antimony pentachloride is a good catalyst; in contrast to the action of aluminum chloride, the process is actually a catalytic one.

4. Antimony pentachloride was also a good catalyst in the reaction with ethyl nitrate. In this case the formation could be observed of an unstable compound of $SbCl_5$ with $C_2H_5NO_2$. This compound is an intermediate product of reaction on the one hand, and may catalyze the reaction of benzene with a fresh quantity of ethyl nitrate on the other hand.

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* See Consultants Bureau Translation, p. 1067.

EPOXY ALCOHOLS (OXIDOLS)

III. PREPARATION AND PROPERTIES OF 2,3-EPOXY-2-METHYL-4-BENZYL-4-PENTANOL

V.I. Pansevich-Kolyada and V.A. Ablova

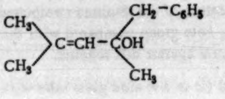
Previous investigations [1, 2] of α,β-epoxy alcohols showed that the properties of the oxide ring of these compounds sharply differed from those of the oxide ring of α-oxides of olefinic hydrocarbons.

Reaction of acetic anhydride with α,β-epoxides of the aliphatic series resulted in acetylation at the hydroxyl group with retention of the oxide ring; heating with fused zinc chloride of α,β-epoxy alcohols caused cleavage into aldehydes and ketones instead of isomerization into carbonyl compounds.

The epoxy alcohol 2,3-epoxy-2-methyl-4-phenyl-4-petnanol [1], containing a phenyl radical at the tertiary alcoholic group, split into acetophenone and isobutyraldehdye even without the action of any reagents when kept in a desiccator over sulfuric acid, calcium chloride or phosphorus pentoxide, and also in dilute sulfuric acid and when heated.

The cause of the special instability of the oxide 2,3-epoxy-2-methyl-4-pentanol was evidently the great accumulation of electronegative groups at the 2, 3 and 4 carbon atoms of the compound. In order, therefore, to obtain a more stable phenyl-containing epoxide, it is evidently necessary to have a certain distance between these groups. As a test of this hypothesis we realized the preparation of the epoxy alcohol 2,3-epoxy-2-methyl-4-benzyl-4-pentanol (I) by oxidation of 2-methyl-4-benzyl-2-penten-4-ol with acetyl hydroperoxide.

We synthesized the alcohol, in a similar manner to Fellenberg [3], by the Grignard reaction from benzylmagnesium chloride and mesityl oxide. It should be noted that, contrary to the categorical assertion of Esafov [4] regarding the absence of normal reaction between benzylmagnesium chloride and mesityl oxide, we obtained 2-methyl-4-benzyl-2-penten-4-ol (II) by this reaction in a yield of up to 60% of the theoretical



$$(CH_3)_2C{=}CH{-}C(OH)(CH_3){-}CH_2{-}C_6H_5$$

(II)

Oxidation of this alcohol was conducted in a solution of anhydrous ether with 65% acetyl hydroperoxide. The products of oxidation partly crystallized. The isolated crystalline substance had m.p. 71.5-72.5°. It was the epoxy alcohol, 2,3-epoxy-2-methyl-4-benzyl-4-pentanol (I).

The latter forms white crystals with a camphor-like odor; unlike, 2,3-epoxy-2-methyl-4-phenyl-4-pentanol, it did not change when kept in a desiccator over sulfuric acid. Heating with acetic anhydride yielded the oxido-acetate with m.p. 121-122°. Acetylation took place at the hydroxyl group with retention of the oxide ring, as in the case of the previously studied alcohol-oxides of the aliphatic series [2].

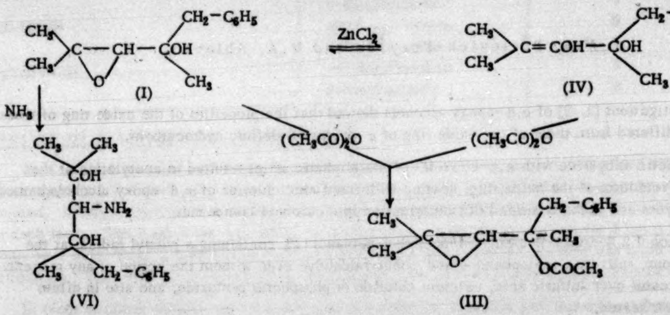
Heating of 2,3-epoxy-2-methyl-4-benzyl-4-pentanol (I) with anhydrous zinc chloride or even with extremely dilute aqueous sulfuric acid led to formation of a substance with m.p. 138-139°.

The quantitative composition of this substance and the epoxy alcohol was the same and corresponded to the formula $C_{13}H_{18}O_2$. Consequently it was a product of isomerization of the epoxy alcohol under the action of fused zinc chloride and dilute sulfuric acid. The substance with m.p. 138-139° did not contain a carbonyl group but contained two hydroxyl groups. This is only possible if our epoxy alcohol had isomerized not to a ketoalcohol but to an unsaturated glycol whose structure most probably corresponds to 2-methyl-4-benzyl-2-penten-3,4-diol (IV).

The same substance was obtained also on vacuum distillation of the mother liquor of the non-crystallizable products of oxidation which remained after separation of the alcohol-oxide.

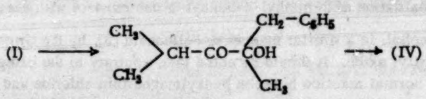
Heating of the unsaturated glycol (IV) with acetic anhydride yields the oxidoacetate (III) with m.p. 121-122°, identical with the product from the epoxy alcohol in the same conditions.

Consequently, the epoxy alcohol – 2,3-epoxy-2-methyl-4-benzyl-4-pentanol (I) – and the isomeric glycol – 2-methyl-4-benzyl-2-penten-3,4-diol (IV) – are individual chemical compounds capable in suitable conditions of mutual transformations with rupture and reduction of the oxide ring. This extremely interesting and previously unobserved phenomenon evidently points to the occurrence of a new form of oxide-enol tautomerism. Both tautomers give one and the same monoacetate (III):



The new tautomeric transformation differs from those previously known in that the enolic form is formed by translocation of hydrogen atom to an oxygen atom not from an adjacent carbon atom but from the one linked to an oxygen atom.

Formation of the unsaturated glycol (IV) may be represented by the following scheme:



$$(I) \longrightarrow (CH_3)_2CH{-}CO{-}C(OH)(CH_2{-}C_6H_5)(CH_3) \longrightarrow (IV)$$

(V)

However, the absence of reactions of the obtained compounds (III and IV) for the carbonyl group and the undoubtedly greater stability of the keto group compared with that of the oxide ring and the hydroxyl group at the double bond are weighty evidence against this scheme.

On heating the epoxy alcohol (I) in a sealed glass tube with aqueous ammonia, an aminodiol is obtained. Krasusky [5] showed that in the formation of aminoalcohols from α-oxides and ammonia, the amino group is usually located at the more hydrogenated carbon atom. Hence the aminoalcohol that we prepared is most probably 2-methyl-4-benzyl-3-amino-2,4-pentanediol (VI).

The present investigation of 2,3-epoxy-2-methyl-4-benzyl-4-pentanol (I) shows that the properties of α,β-epoxy alcohols are determined not only by the presence and position of their functional groups but also by the radicals attached to the oxidized carbon atoms. Remoteness of the phenyl radical from the tertiary alcohol group stablizes the carbon skeleton of the epoxy alcohol (I), in which respect it differs both from epoxy alcohols of the aliphatic series and from the epoxy alcohol, 2,3-epoxy-2-methyl-4-phenyl-4-pentanol, in which the phenyl radical is attached directly to the carbon atom of the tertiary alcohol group. Unlike this epoxy alcohol, the epoxy alcohol (I) did not undergo modification when kept in a desiccator over sulfuric acid, while it was not cleaved under the action of anhydrous zinc chloride as was the case with epoxy alcohols of the aliphatic series, but was only isomerized to the unsaturated glycol (IV). With ammonia the epoxy alcohol (I), like α-oxides of the olefinic hydrocarbons, forms an aminodiol (VI). Finally, due to the stabilization of the carbon skeleton of the α,β-epoxy alcohol (I), it was possible to establish interesting intramolecular transformations. These tautomeric transformations are possibly also characteristic of other epoxy alcohols, but due to the instability of their molecules they apparently proceed at such a velocity that their observation is greatly hindered.

EXPERIMENTAL

Preparation of 2-methyl-4-benzyl-2-penten-4-ol (II)

To 6 g magnesium in anhydrous ether was slowly added 31.6 g benzyl chloride. After heating for an hour, the mixture was cooled and dropwise addition was made of 24.5 g mesityl oxide with cooling. An energetic reaction took place. After addition of the whole amount of mesityl oxide, the mixture was heated for an hour on a water bath and then left overnight. The magnesium complex was decomposed at first with ice and then with saturated NH_4Cl solution. The ethereal solution of the reaction products was dried with potassium carbonate, the ether was driven off, and the alcohol was distilled in vacuum:

b.p. 120-122° at 9 mm; n_D^{20} 1.5186; d_4^{20} 0.9645; MR_D 59.75; calculated 59.69.

0.1543 g sub.: 0.4646 g CO_2; 0.1310 g H_2O. Found %: C 82.16; H 9.50. $C_{13}H_{18}O$. Calculated %: C 82.10; H 9.47.

Oxidation of 2-methyl-4-benzyl-2-penten-4-ol with acetyl hydroperoxide

To 62 g alcohol (II) in 130 ml anhydrous ether was slowly added 39 g 65% acetyl hydroperoxide. Oxidation proceeded quietly without much heat development. The temperature of the mixture was held at 20-25°.

The next day the reaction mixture contained 0.44 g unreacted acetyl hydroperoxide. The acetic acid was neutralized first with sodium carbonate solution and then with dry sodium carbonate. The ethereal solution was dried over $MgSO_4$. After removal of the ether in vacuum, crystallization commenced. 17 g of white crystalline substance with a camphor-like odor was obtained with m.p. (after recrystallization from ethanol) of 71.5-72.5°. The substance was soluble in benzene, isomyl ether, and methyl and ethyl alcohols. It displaced iodine from potassium iodide in acetic acid solution.

0.1331 g substance: 0.3702 g CO_2; 0.1059 g H_2O. 0.1255 g substance: 15.8 ml CH_4 (0°, 760 mm). 0.1204, 0.2134 g substance: 17.39 g benzene: Δt 0.179, 0.312°. Found%: C 75.90, H 8.91; OH 9.60; M 198.8, 201.2. $C_{13}H_{18}O_2$. Calculated %: C 75.75; H 8.74; OH 8.20; M 206.

The liquid portion of the oxidation products was distilled at 5 mm to give the following fractions: 1st frac. b.p. 104-115°; 2nd b.p. 115-119°; 3rd b.p. 119-122°; 4th b.p. 122-130°; 5th b.p. 133-152°.

The second fraction crystallized completely. After recrystallization from ethanol it formed white, fluffy needles with m.p. 138-139°.

0.1370 g sub.: 0.3779 g CO_2; 0.1127 g H_2O. 0.0621 g sub.: 14.28 ml CH_4 (0°, 760 mm). Found %: C 75.30; H 9.20; OH 17.57. $C_{13}H_{18}O_2$. Calculated %: C 75.75; H 8.74; OH 16.5.

The third fraction partly crystallized. The crystals melted at 71.5-72.5° after recrystallization from ethanol.

Reaction of 2,3-epoxy-2-methyl-4-benzyl-4-pentanol with acetic anhydride

4 g alcohol-oxide (I) and 10 g acetic anhydride were heated for 3 hours on a water bath and were then boiled for 10 hours. The acetic anhydride was distilled off in vacuum and the acetylation product was distilled at 4 mm to give the following fractions: 1st frac. b.p. 85-135°; 2nd frac. b.p. 135-155°, 3rd frac. b.p. 155-157° 2.6 g.

The third fraction crystallized to form fine needles, sparingly soluble in ether and ethanol, readily in benzene. After recrystallization from ethanol they melted at 121-122°. The substance did not give a reaction for the carbonyl group; an impurity containing active hydrogen was present (1.52% calculated on hydroxyl). It displaced iodine from potassium iodide in acetic acid solution.

0.1162 g sub.: 0.3050 g CO_2; 0.0810 H_2O. 0.0948 g sub.: 1908 g benzene: Δt 0.106°. Found %: C 71.63; H 8.09; M 240.9. $C_{15}H_{20}O_3$. Calculated %: C 72.58; H 8.02; M 248.

Action of Sulfuric Acid on 2,3-epoxy-2-methyl-4-benzyl-4-pentanol

1.5 g alcohol-oxide (I) was heated on a water bath with dilute sulfuric acid. At the outset the crystals melted but later crystallized in the form of white, coalescent needles, which after recrystallization from ethanol melted at 138-139°. No depression with the product of treatment with zinc chloride (see below).

Action of zinc chloride on 2,3-epoxy-2-methyl-4-benzyl-4-pentanol

2 g (I) and 0.4 g zinc chloride were heated on a water bath. The alcohol-oxide melted and later the whole mass crystallized. No evolution of volatile substances. The substance is soluble with heating in ethanol, and in the cold the same solution deposits long needles, m.p. 138-139°, sparingly soluble in benzene.

0.1120 g substance: 0.3088 g CO_2; 0.0873 g H_2O. 0.0517 g substance: 10.28 ml CH_4 (0°, 760 mm). 0.0988 g substance: 20.03 g benzene: Δt 0.122°. Found %: C 75.24; H 8.73; OH 15.18; M 207.8. $C_{13}H_{18}O_2$. Calculated C 75.75; H 8.74; OH 16.5; M 206.

Reaction of 2-methyl-4-benzyl-2-penten-3,4-diol with acetic anhydride

To 0.9 g glycol (IV) with m.p. 138-139°, obtained by the action of dilute sulfuric acid on 2-epoxy-2-methyl-4-benzyl-4-pentanol (I), was added 5 g acetic anhydride, and the mixture was heated 2 hours on a water bath and then boiled for an hour on a hotplate. The substance dissolved on heating with acetic anhydride and the color changed to yellow. The next day the acetic anhydride was taken off in vacuum and the residue crystallized. Yield 0.35 g with m.p. 121-122°. A mixed test with compound (III), obtained by the action of acetic anhydride on 2,3-epoxy-2-methyl-4-benzyl-4-pentanol, did not give a depression of melting point.

Reaction of 2,3-epoxy-2-methyl-4-benzyl-4-pentanol with ammonia

2 g alcohol-oxide (I) and 30 ml saturated aqueous ammonia were heated in a sealed glass tube at 90-100° for 6 hours. After driving off the ammonia, the reaction product was extracted with ether and the extract dried over $MgSO_4$. The ether was distilled off and the substance recrystallized from hot hexane. The crystals were slender, fine needles melting at 116-117°. Readily soluble in inorganic acids and organic solvents. Nitrogen and active hydrogen were present.

0.1294 g sub.: 6.98 ml N_2 (0°, 760 mm). 0.0747 g sub.: 20.95 g benzene: Δt 0.083°. 0.0740 g sub.: 29.3 ml CH_4 (0°, 760 mm). Found %: N 6.75; active H 1.78; M 220.8. $C_{13}H_{21}O_2N$. Calculated %: N 6.28; active H 1.79; M 223.

SUMMARY

1. Oxidation of 2-methyl-4-benzyl-2-penten-4-ol with acetyl hydroperoxide gives the oxidol, 2,3-epoxy-2-methyl-4-benzyl-4-pentanol, which with acetic anhydride gives the oxido-acetate, 2,3-epoxy-2-methyl-4-benzyl-4-acetoxy-pentane.

2. Heating of 2,3-epoxy-2-methyl-4-benzyl-4-pentanol with anhydrous zinc chloride or dilute sulfuric acid gave the unsaturated glycol, 2-methyl-4-benzyl-2-penten-3,4-diol. With acetic anhydride this glycol gives the same oxido-acetate as was obtained from the oxide-alcohol.

3. 2,3-Epoxy-2-methyl-4-benzyl-4-pentanol reacts with ammonia to form the aminodiol, 2-methyl-4-benzyl-3-amino-2,4-pentanediol.

4. The epoxy alcohol and the unsaturated glycol are individual substances capable of undergoing mutual transformations in appropriate conditions with rupture and reduction of the oxide ring. This transformation may be described as oxido-enol tautomerism.

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* See Consultants Bureau Translation, p. 1437.

** " " " " p. 21.

COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XI. REACTION OF ETHYL β-METHYL-β-ETHYLGLYCIDATE WITH o- AND p-TOLUIDINE

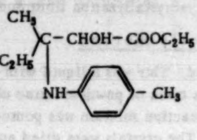
V.F. Martynov and Ya. A. Kastron

In one of the previous communications [1] we described the reaction of ethyl β-methyl-β-ethylglycidate with aniline.

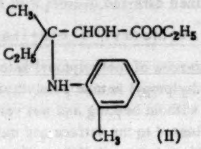
Our present investigation is a continuation of this research. Addition of p-toluidine to the above-mentioned ester of glycidic acid was effected in the usual manner, i.e. by heating the mixture of reactants in a sealed ampoule at 170-180°. The reaction product was obtained in sufficiently good yield. This method proved less suitable, however, for o-toluidine. Steric hindrance, due to the methyl group of o-toluidine, caused the reaction to proceed with difficulty. 50 hours heating in the above-mentioned conditions completely failed to yield the anticipated reaction product.

It must be pointed out that in similar conditions the reaction between o-toluidine and ethyl β,β-ethylglycidate took place with a good yield, [2]. In order to effect the addition of o-toluidine to ethyl-β-methyl-β-ethyl glycidate, we resorted to more drastic conditions. The mixture of components (excess of o-toluidine) was heated to the boil over Wood's alloy in a flask fitted with a reflux condenser protected against atmospheric moisture by a Tishchenko flask containing sulfuric acid. During the process the temperature rose to approximately 200° (the b.p. of o-toluidine). But even in these conditions after 10 hours' heating we obtained a very low yield (11%) of addition product. And only after 22 hours' heating did the reaction proceed with a fully satisfactory yield.

On the basis of all the preceding studies we can ascribe to both products the structure of the ethyl ester of α-hydroxy-β-(o,p-toluidino)-isocaproic acid.

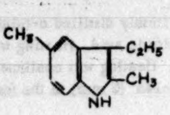


(I)

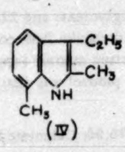


(II)

With the objective of conclusively demonstrating the structure of both of the products that we prepared (I and II), we subjected them to the action of conc. sulfuric acid. As had been expected, evolution of carbon monoxide was observed and conclusively showed that we were indeed dealing with α-hydroxy-β-amino acids. The fragments of the molecules after splitting-off of carbon monoxide should be stablized by transformation into the corresponding indole homologs; on the basis of the preceding investigation [1], it was to be expected that the ethyl ester of α-hydroxy-β-(p-toluidino)-isocaproic acid (I) would after loss of carbon monoxide be transformed into 2,5-dimethyl-3-ethylindole (III), while the ethyl ester of α-hydroxy-β-(o-toluidino)-isocaproic acid should give 2,7-dimethyl-3-ethylindole (IV):



(III)



(IV)

We actually obtained substances the data for which corresponded with the above-mentioned indole homologs. The compound to which we attributed the structure (III) formed colorless, scaly crystals which deliquesced and darkened after a few days. Compound (IV) formed a colorless liquid which darkened relatively quickly in the air.

For conclusive proof of their structure we synthesized 2,5-dimethyl-3-ethylindole by A.E. Arbuzov's method [3] and obtained the same scaly crystals with the same melting point which darkened and deliquesced after a few days. The picrate of the authentic 2,5-dimethyl-3-ethylindole melted at the same temperature as the picrate of the compound that we prepared. No melting point depressions were observed in mixed tests either with the compounds themselves or their picrates. Consequently the structure of compound (III) can be said to be conclusively demonstrated. Concerning compound (IV), we may claim on the basis of our previous investigation [1] and of the foregoing data that its structure undoubtedly corresponds to 2,7-dimethyl-3-ethylindole.

EXPERIMENTAL

Ethyl α-hydroxy-β-(p-toluidino)-isocaproate

40 g ethyl β-methyl-β-ethylglycidate in admixture with 27 g freshly distilled p-toluidine (molar ratio) was heated in a sealed ampoule for 25 hours at 170-180°. The reaction mass was a viscous, light-yellow liquid. Vacuum distillation at 3 mm gave a fraction with b.p. 149-153° in the form of a very viscous, light-yellow liquid which rapidly crystallized; yield 37 g (55 %).

Three recrystallizations from ligroine gave a colorless, finely crystalline powder with m.p. 57-58°.

0.2187 g sub.: 10.1 ml N_2 (21°, 760.6 mm); 0.3948 g sub.: 18.5 ml N_2 (20°, 744.1 mm). Found %: N 5.32, 5.28. $C_{15}H_{23}O_3N$. Calculated %: N 5.28

Synthesis of 2,5-dimethyl-3-ethylindole

5.5 g ethyl α-hydroxy-β-(p-toluidino)-isocaproate was introduced into 35 ml conc. sulfuric acid and heated over a bare flame. Mutual solution of the substances occurred with progressive heating and the liquid acquired a straw-yellow color. At 85° (thermometer in reaction mixture) bubbles of carbon monoxide started to come off and this process became very intensive at 115°. As soon as carbon monoxide evolution had ceased, the reaction mass (without preliminary cooling) was poured into iced water; scaly crystals separated and were collected, washed with water and recrystallized from aqueous ethanol. Light-yellow scales with m.p. 65-66° were obtained. The yield was nearly quantitative.

0.1361 g sub.: 9.8 ml N_2 (20°, 750.3 mm). 0.0787 g sub.: 5.7 ml N_2 (20°, 750.8 mm). Found %: N 8.13, 8.18. $C_{12}H_{15}N$. Calculated %: N 8.09.

The picrate formed dark-red needles with m.p. 144-145° after recrystallization from aqueous ethanol.

Synthesis of 2,5-dimethyl-3-ethylindole by Arbuzov's method

The p-tolylhydrazone of methylpropyl ketone was first prepared. This was a liquid with b.p. 120-122° at 2 mm. To 8 g methylpropyl ketone p-tolylhydrazone was added a trace of powdered zinc chloride. The reaction commenced without heating and was very energetic. The reaction mixture was poured into cold water; an oily layer floated to the surface and quickly crystallized. The crystals were dried and distilled in vacuum; b.p. 130-132° at 4 mm. A light-yellow liquid was obtained which quickly crystallized. The yield was nearly quantitative. Recrystallization from aqueous alcohol gave lustrous scales with m.p. 64-65°.

0.2020 g sub.: 14.8 ml N_2 (27°, 768 mm). Found %: N 8.19. $C_{12}H_{15}N$. Calculated %: N 8.09.

The picrate formed dark-red needles with m.p. 143-145° (from aqueous ethanol).

A mixed test of the indoles obtained by the two methods did not give a m.p. depression. A mixed sample of the picrates also melted without depression.

Ethyl α-hydroxy-β-(o-toluidino)-isocaproate

19.5 g ethyl β-methyl-β-ethylglycidate and 22 g (excess) freshly distilled o-toluidine were heated under a reflux condenser closed with a Tishchenko flask containing sulfuric acid. Heating was effected on a bath of Wood's alloy to the b.p. of the reaction mixture (approx. 205°). Heating was continued for 22 hours with interruptions. The anticipated reaction product was distilled at 143-145° (2 mm) in the form of a viscous, light-yellow liquid. Yield 19 g (58 %).

d_4^{20} 1.0760; n_D^{20} 1.5280; MR_D 75.90; Calculated 74.64; EM_D 1.26.

0.1556 g sub.: 7.2 ml N_2 (18°, 764.5 mm): 0.1595 g sub.: 7.8 ml N_2 (21°, 745.4 mm). Found %: N 5.37, 5.44. $C_{15}H_{23}O_3N$. Calculated %: N 5.28.

Synthesis of 2,7-dimethyl-3-ethylindole

13 g ethyl α-hydroxy-β-(o-toluidino)-isocaproate was mixed with 35 ml conc. sulfuric acid. The mixture was heated over a bare flame. At 103° (thermometer in the reaction mixture) bubbles of carbon monoxide started to come off and the process was especially intensive at 110-115°. Carbon monoxide continued to come off for 40-45 minutes and the solution acquired a cherry red color.

After gas had ceased to come off, the mixture was poured into iced water. The reaction product was extracted with ether and then vacuum-distilled. B.p. 123-126° (3 mm). Yield 5 g (59 %).

d_4^{20} 1.0188; n_D^{20} 1.5848; MR_D 56.98; Calculated 54.94; EM_D 2.04. 0.2121 g sub.: 14.8 ml N_2 (15°, 762.2 mm). 0.0998 g sub.: 7.0 ml N_2 (16°, 762 mm). Found %: N 8.18, 8.23. $C_{12}H_{15}N$. Calculated %: N 8.09.

SUMMARY

1. The reaction of ethyl β-methyl-β-ethylglycidate with o- and p-toluidine was investigated. The opening of the oxide ring of the acid was shown to take place from the side of the tertiary β-carbon atom. The previously undescribed ethyl α-hydroxy-β-(p-toluidino)-isocaproate and ethyl α-hydroxy-β-(o-toluidino)-isocaproate were synthesized.

2. Transition was effected from ethyl α-hydroxy-β-(p-toluidino)-isocaproate to 2,5-dimethyl-3-ethylindole, and from ethyl α-hydroxy-β-(o-toluidino)-isocaproate to 2,7-dimethyl-3-ethylindole. Neither of these homologs of indole has been described in the literature.

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* See Consultants Bureau Translation, p. 1637.

** " " " " p. 1033.

HYDROGENATION WITH COLLOIDAL PALLADIUM IN PRESENCE OF INHIBITORS

IV. HYDROGENATION OF METHYL-PHENYL-ETHYNYL CARBINOL

Kh. V. Balyan

In previous communications [1,2] we described the results of our investigations of the hydrogenation with colloidal Pd of acetylenic alcohols, γ-glycol and olefinic alcohols, as well as of the methyl ether of dimethyl-ethynyl carbinol and dimethyl-vinyl carbinol in presence of some organic additives. Some of the latter had a retarding effect upon the course of hydrogenation; others were accelerators. The degree of inhibition in the first and second stage of hydrogenation often differed, thus pointing to a selectivity of the process.

It appeared of interest to follow the course of hydrogenation in presence of inhibitors of analogous compounds with an aromatic radical. For this purpose we selected methyl-phenyl-ethynyl carbinol, the hydrogenation of which, generally speaking, has not been investigated.

The hydrogenation procedure did not differ from that described in previous communications. The hydrogenation products were qualitatively and quantitatively analyzed for compounds with a double and a triple bond.

The olefinic bond was qualitatively determined with the help of bromine water, and the acetylenic bond with an ammoniacal solution of silver oxide or cuprous chloride. Furthermore, for determination of the acetylenic bond we made use of a new test with metallic sodium.

Not devoid of interest was the observation of the differing behavior of methyl-phenyl-ethynyl carbinol and its aliphatic analogs – dimethyl-ethynyl carbinol and methyl-ethyl-ethynyl carbinol toward ammoniacal silver oxide and cuprous chloride. The first alcohol gives a white precipitate of the silver derivative both in aqueous solution and in a solution in methanol or ethanol. The aliphatic analogs, however, do not give corresponding precipitates in methanol or ethanol.

Dimethyl-ethynyl carbinol and methyl-ethyl-ethynyl carbinol do not give characteristic precipitates of copper derivatives in aqueous solutions with an ammoniacal solution of cuprous chloride. At low concentrations of these alcohols, precipitates are not formed even in alcoholic solutions. Methyl-phenyl-ethynyl carbinol, however, gives a characteristic white or yellowish precipitate (depending on the concentration of the alcoholic solutions) not only in aqueous [3] but also in alcoholic solutions.

The metallic sodium test for the triple bond is based on the observation of Zalkind and Bukhovets [4] that heating of γ-acetylenic glycols in alcoholic solution with metallic sodium results in cleavage of the glycol with separation of free acetylene. The latter may be detected with ammoniacal cuprous chloride. We have successfully applied this reaction to acetylenic alcohols, which proved to be extremely sensitive to it. It enabled, for example, 6-10 mg methyl-phenyl-ethynyl carbinol to be detected in solution in 3-4 ml methanol.*

Olefinic compounds were qualitatively determined by the bromate-bromide method [5] and acetylenic compounds with the help of silver nitrate. By this method the original methyl-phenyl-ethynyl carbinol was found to be 99.21% pure.

Methyl-phenyl-ethynyl carbinol was first hydrogenated with an equimolar amount of hydrogen in the absence of inhibitor.

Qualitative and quantitative analysis of the hydrogenation products revealed complete or nearly complete absence of triple-bond compounds. Analysis for double bonds showed that 95.40% methyl-phenyl-vinyl carbinol was present. It can, therefore, be concluded that methyl-phenyl-ethynyl carbinol is strictly selectively hydrogenated in presence of colloidal Pd, i.e. the first two hydrogen atoms add on exclusively at the triple bond. It thus behaves like monosubstituted tertiary acetylenic alcohols of the aliphatic series in presence of palladium precipitated on calcium carbonate [6]. On the other hand, the behavior of methyl-phenyl-ethynyl carbinol differs markedly in this respect from that of dimethyl-phenyl-ethynyl carbinol and diphenyl-phenyl-ethynyl carbinol, which (according to Zalkind) are not selectively hydrogenated in these conditions [7].

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* This reaction was also found to be applicable to acetylenic-olefinic alcohols of the type of $R_2C(OH)-C\equiv C-CH=CH_2$, where R is methyl or ethyl. When heated with sodium, these alcohols split into the corresponding ketones and vinylacetylene which can be qualitatively detected by the same cuprous chloride and quantitatively determined with an alkaline solution of mercuric iodide in potassium iodide.

Parallel experiments were run on hydrogenation of methyl-phenyl-ethynyl carbinol with the same catalyst but in the presence of some inhibitors previously used by us (Table 1).

TABLE 1

No.	Name of inhibitor	Duration of addition of 2H (in min.)	Inhibition during first half of hydrogenation	Content (in %) of methyl-phenyl-ethynyl carbinol	Content (in %) of methyl-phenyl-vinyl carbinol
1	Without inhibitor	5.5; 3.5 *	-	0.76	95.40
2	Without inhibitor**	21 **	-	0	0
3	p-Thiocyanochlorobenzene**	20-30; 130**	4-6 times and 6-7 times in the second half	0	0
4	p-Thiocyanoaniline	9	1 and a half times	3.75	91.83
5	Phenyl mustard oil	18	3 times	0	94.33
6	Chlorobenzene	9	1 and a half times	0	92.64
7	Thiocyano-1-naphthol***	7	2 times	2.74	93.72
8	p-Thiocyanochlorobenzene	30	5 times	4.05	94.29

The influence of inhibitors is shown in Table 1 and Figures 1,2 and 3. The greatest retardation (4-6 times) is caused by p-thiocyanochlorobenzene. A hydrogenation experiment with 0.4 mg p-thiocyanochlorobenzene (0.054%) on the weight of methyl-phenyl-ethynyl carbinol) showed that this amount of inhibitor completely poisons the catalyst, and after 40 minutes not a single milliliter of hydrogen had combined. With a twofold reduction in the amount of this inhibitor (0.2 mg, 0.027%) on the weight of alcohol), hydrogenation took place but very slowly (retardation by a factor of approx. 6 both in the first and in the second stage of hydrogenation).

Results of quantitative analysis of the products of hydrogenation are set forth in Table 1 which shows that the action of chlorobenzene and phenyl mustard oil hardly modifies the composition of the hydrogenation products obtained in the absence of inhibitor. The remaining inhibitors only slightly worsen the selective character of the hydrogenation, leaving from 2.74 to 4.05% of the methyl-phenyl-ethynyl carbinol unreacted. On addition of 2 moles hydrogen to 1 mole acetylenic alcohol, alcohols with a triple or double bond were not detected in the products of hydrogenation.

The product of partial hydrogenation of methyl-phenyl-ethynyl carbinol (methyl-phenyl-vinyl carbinol) was obtained for the first time by Lebedeva and Shlyakova [5]. Methyl-phenyl-vinyl carbinol prepared by us was a perfectly colorless oil free from odor; a triple bond was not detected; the bromate-bromide method indicated a 93.04% content of double-bond compound. The product was obtained in 86% yield. Consequently the hydrogenation of methyl-phenyl-ethynyl carbinol is an extremely convenient method for the preparation of methyl-phenyl-vinyl carbinol.

EXPERIMENTAL****

Methyl-phenyl-ethynyl carbinol was prepared by Zalkind's method [3]; m.p. 50-50.5°.

0.0254 g methyl-phenyl-ethynyl carbinol, 5 ml methanol, 100 ml 2% $AgNO_3$; 1.72 ml KOH (T 0.005630). Indicator was methyl red. Found methyl-phenyl-ethynyl carbinol 0.0252 g, i.e. 99.21% content of pure substance.

Results of quantitative anaylsis of the hydrogenation products are set forth in Table 2.

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* First value with 2 mg Pd and the second with 3 mg Pd.

** Hydrogenation took 4H per mole alcohol.

*** Hydrogenated with 3 mg Pd.

**** Quantitative analyses were carried out by L.L. Cherenkova.

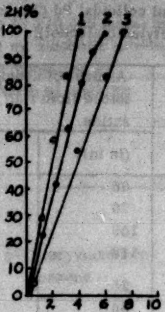

Fig. 1. Hydrogenation of methyl-phenyl-ethynyl carbinol with colloidal palladium

1) with 3 mg catalyst;
2) with 2 mg catalyst;
3) with 2 mg catalyst and 0.2 mg thiocyano 1-naphthol

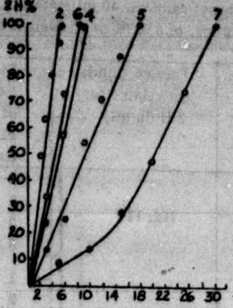

Fig. 2. Hydrogenation of methyl-phenyl-ethynyl carbinol with 2 mg colloidal Pd in presence of inhibitors (see Table 3)

2) with inhibitors; 4) with 0.2 mg p-thiocyanoaniline; 5) with 0.2 mg phenyl mustard oil; 6) with 0.2 mg chlorobenzene; 7) with 0.2 mg p-thiocyanochlorobenzene.

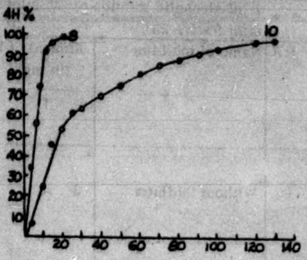

Fig. 3. Hydrogenation of methyl-phenyl-ethynyl carbinol with 2 mg colloidal palladium (see Table 3).

8) without inhibitor;
10) with 0.2 mg p-thiocyanochlorobenzene.

TABLE 2

Analysis of Products of Hydrogenation of Methyl-phenyl-ethynyl Carbinol

(Hydrogenation was effected with 2 H per Mole of Acetylenic Alcohol)

No.	Name of inhibitor	Wt.of methyl-phenyl-ethynyl carbinol (in g)	Consumption of alkali as 0.1 N solution (in ml)	Total content of triple-bond compound (in %)*	Consumption of bromate-bromide as 0.2 N solution (in ml)	Total content of double-bond compound (in %) *
1	Without inhibitor	1.46	0.765	0.76	95.40	95.40
2	Thiocyano-1-naphthol	1.46	2.74	2.74	93.72	93.72
3	Thiocyanoaniline	1.46	3.75	3.75	91.83	91.83
4	Phenyl mustard oil	1.46	0	0	94.33	94.33
5	Chlorobenzene	1.46	0	0	92.64	92.64
6	p-Thiocyanochlorobenzene	1.46	4.05	4.05	94.29	94.29
7	Unhydrogenated methyl-phenyl-ethynyl carbinol	0.0254	1.73	99.21	–	–
8	Without inhibitor**	0.73	0	0	0	0
9	p-Thiocyanochlorobenzene**	0.73	0	0	0	0

---

* The percentage of triple-bond compound was related to the original weight of methyl-phenyl-ethynyl carbinol; that of double-bond compound was related to the theoretical yield of methyl-phenyl-vinyl carbinol (1.48 g) on the basis of the original weight.

** Hydrogenated with 4 H per mole alcohol.

TABLE 3

0.73 g (0.005 mole) methyl-phenyl-ethynyl carbinol, 40 ml methanol, 2 or 3 ml colloidal Pd (2 or 3 mg Pd), 1 ml alcoholic solution of inhibitor (0.2 mg, or 0.027% of the weight of the acetylenic alcohol); temperature 20°.

No.	Name of inhibitor	Amount of Pd (in mg)	Pressure (mm); calculated for 2 H (in ml)	Duration from start of hydrogenation (in min.)	Amount of hydrogen absorbed from start of reaction (in ml)	Amount of hydrogen absorbed from start of reaction (in %)
1	Without inhibitor	3	762; 119	1	35	29.41
				2	70	58.82
				3	100	84.03
				3.5	119	100.0
2	Without inhibitor	2	776;118	1	25	21.18
				2	50	42.37
				3	75	63.56
				4	95	80.51
				5.5	118	100.0
3	Thiocyano-1-naphthol	3	762;119	2	40	33.61
				4	65	54.61
				6	100	84.03
				7	120	100.85
4	p-Thiocyanoaniline	2	758;120	3	28	23.37
				6	70	58.33
				9	120	100.0
5	Phenyl mustard oil	2	758;120	3	15	12.50
				6	30	25.0
				9	65	54.17
				12	85	70.84
				15	105	87.50
				18	120	100.0
6	Chlorobenzene	2	758;120	3	39	32.50
				6	88	73.17
				9	120	100.0
7	p-Thiocyanochlorobenzene	2	763; 120	5	10	8.33
				10	17	14.17
				15	33	27.50
				20	57	47.50
				25	90	75.0
				30	122	101.80
8	Without inhibitor	2	759; 120 and 759;4H-240	3	80	33.33*
				6	135	56.25
				9	180	75.0
				12	220	91.67
				15	232	96.67
				18	238	99.15
				21	238	99.15
9	p-Thiocyanochlorobenzene**	2	759; 120 and 4H-240	10	0	0
				20	0	
				30	0	
				40	0	

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* Calculated when starting from 240 ml hydrogen.

** 0.4 mg taken.

(Table continued on following page)

TABLE 3 (Continued)

0.73 g (0.005 mole) methyl-phenyl-ethynyl carbinol, 40 ml methanol, 2 or 3 ml colloidal Pd (2 or 3 mg Pd), 1 ml alcoholic solution of inhibitor (0.2 mg, or 0.027%) of the weight of the acetylenic alcohol); temperature 20°.

No.	Name of inhibitor	Amount of Pd (in mg)	Pressure (mm): calculated for 2 H (in ml)	Duration from start of hydrogenation (in min.)	Amount of hydrogen absorbed from start of reaction	
					(in ml)	(in %)
10	p-Thiocyanochlorobenzene	2	759; 120 and 4H - 240	10	60	25.00
				20	130	54.17
				30	153	63.75
				60	195	81.23
				90	220	91.67
				120	236	98.34
				130	239	99.60
11	Without inhibitor*	10	769; 720	2	290	40.24
				4	535	74.30
				6	720	100.0

Hydrogenation of methyl-phenyl-ethynyl carbinol was carried out in the same conditions and with the same apparatus as in the previous communications [1,2].

Results of some experiments on hydrogenation of methyl-phenyl-ethynyl carbinol are set forth in Table 3.

After hydrogenation (expt. 11) the solution was filtered from catalyst and the filter was washed with methanol; the methanol was distilled off and the residual slightly yellow oil was dissolved in ether. The ethereal solution was dried with calcined potassium carbonate, the ether was driven off, and the residual oil distilled in vacuum (0.5 mm). The colorless, transparent oil came over at exactly 62°. A residue of 0.48 g yellow oil in the distillation flask was not investigated.

Amount of product with b.p. 62° (0.5 mm) 3.82 g (86%); d_{20}^{20} 1.0114; d_4^{20} 1.0095 n_D^{20} 1.5338.

According to the literature [5], methyl-phenyl-vinyl carbinol has b.p. 89-90° (5 mm); d_4^{21} 0.9965; n_D^{21} 1.52772; the double-bond content by the bromide-bromate method was 89-90%.

Qualitative anaylsis (with metallic sodium) and quantitative analysis did not reveal the presence of any triple-bond compounds.

Analysis for double bond: 1.1045 g substance, 5 ml methanol, 10 ml water, 3 ml 4 N HCl: 12.5 ml bromate-bromide (T 0.005557); 10 ml 10% KI, 12 ml thiosulfate (T 0.02438, indicator starch solution). Found: methyl-phenyl-vinyl carbinol 0.09723 g (93%).

SUMMARY

1. It was established that methyl-phenyl-ethynyl carbinol, unlike dimethyl-phenyl-ethynyl carbinol and diphenyl-phenyl-ethynyl carbinol, is hydrogenated strictly selectively in presence of colloidal palladium with formation of methyl-phenyl-vinyl carbinol. The method of hydrogenation of methyl-phenyl-ethynyl carbinol for preparation of the vinyl compound has undoubted advantages (speed, purity of product, and high yield of 86%) over other methods.

2. It is shown that some organic compounds thiocyano-α-naphthol, p-thiocyano-aniline, phenyl mustard oil, chlorobenzene, p-thiocyanochlorobenzene - taken in the amount of 9.927% of the weight of methyl-phenyl-ethynyl carbinol, to a greater or lesser degree retard the hydrogenation; p-thiocyanochlorobenzene is particularly effective.

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* Methyl-phenyl-ethynyl carbinol was taken in quantity of 4.38 g (0.03 mole); the character of the hydrogenation of this alcohol in quantity of 1.46 g without inhibitor and with inhibitor is analogous to the preceding experiments, and, therefore, is not cited here. The composition of the hydrogenation products is given in Table 2.

Unlike other cases of inhibition, however, this inhibiting action either does not affect the selectivity of hydrogenation or only affects it to a very slight extent.

3. It was established that the test with metallic sodium is an extremely convenient and trustworthy reaction for detecting the presence of acetylenic alcohols.

4. The behavior of methyl-phenyl-ethynyl carbinol toward ammoniacal cuprous chloride differs markedly from that of acetylenic alcohols of the aliphatic series — di methyl-ethynyl carbinol and methyl-ethyl-ethynyl carbinol; the first-mentioned compound gives a characteristic precipitate of the copper derivative; the other two do not.

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* See Consultants Bureau Translation, pp. 793 ff.

** " " " " p. 1285.

IMIDAZOLE DERIVATIVES

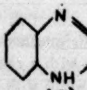
XII. OXIDATION OF 1,2-NAPHTHIMIDAZOLE [1]

B.A. Porai-Koshits, L.N. Kononova and L.S. Efros

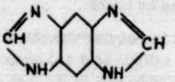
In previous investigations [2,3,4] it was shown that the imidazole ring present in a molecule consisting of condensed rings upsets the bond equivalence of the adjacent rings in the same manner as the benzene ring, for example in naphthalene. In regard to upsetting of bond equivalence, 1,2,4,5-diimidazolo-benzene (II) may thus be compared with anthracene, and benzimidazole (I) with naphthalene.

It was to be expected that this effect of the imidazole ring would also be manifested in the naphthimidazole series. And indeed, not only 1,2,4,5-diimidazolo-benzene (II), but also 2,3-naphthimidazole (III) are reminiscent of anthracene in their properties [5].

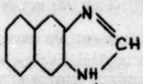
In regard to 1,2-naphthimidazole (IV), whose chemical properties should resemble those of phenanthrene, the literature data are at variance with this hypothesis. Thus, Fischer [6] showed that 1,2-naphthimidazole behaves on oxidation like naphthalene and forms benzimidazole-4,5-dicarboxylic acid (V) - the analog of phthalic acid:



(I)



(II)



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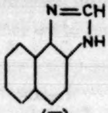

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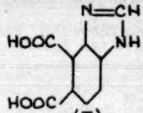


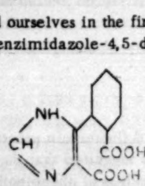
(V)

Fischer appeared to have conclusively demonstrated the structure of this acid by preparing its ester, anhydride, silver salt, anilide, and dyes qualitatively similar to the known phenolphthalein and fluorescein.

Since according to our theory the most unsaturated bond in 1,2-naphthimidazole must be the 3-4 bond, and oxidation of this product should consequently take place at this bond, we decided to repeat Fischer's experiments and to check the accuracy of his conclusions.

It was found that after introducing more precision into the conditions of carrying out of the oxidation of 1,2-naphthimidazole, a substance is obtained which possesses the same properties as were described by Fischer for benzimidazole-4,5-dicarboxylic acid. Its molecular weight (determined by potentiometric titration), however, was high in comparison with that calculated for (V) (234 instead of 206). Also inconsistent with this formula ($C_9H_6O_4N_2$) were our results for elementary analysis (the latter differed considerably from those given by Fischer). At the same time the values found for molecular weight and elementary composition very closely agreed with those for the dicarboxylic acid of structure (VI) whose formation is consistent with our above-enunicated theoretical considerations about the similarity of 1,2-naphthimidazole to phenanthrene. Since, however, we did not consider that the foregoing data constituted an adequate refutation of Fischer's results, we decided to engage in a more detailed study of the derivatives formed from the compound obtained by oxidation of 1,2-naphthimidazole.

We occupied ourselves in the first instance with the properties of the product which Fischer assumed to be the anhydride of benzimidazole-4,5-dicarboxylic acid (VII):



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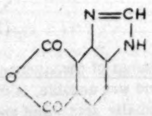
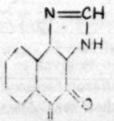


(VII)



(VIII)

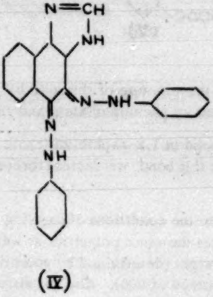
This substance with m.p. 225°, formed by sublimation of the dicarboxylic acid obtained by oxidation of 1,2-naphthimidazole, contained much less nitrogen than was required by formula (VII). The most significant fact, however, was that it was impossible by any means to reconvert it into the original dicarboxylic acid. This substance could be recrystallized from water and it could even be precipitated from alkali solutions with acids in the cold and recovered unchanged. After heating with alkali, however, a new compound crystallized from the acidified solution with a melting point after purification of 203°. After determination of the molecular weight, it was identified as phthalic acid. It was also established that when heated with aqueous alkalies, this "anhydride" evolves ammonia which can be quantitatively collected; the percentage of nitrogen found by this method in the "anhydride" agrees exactly with that found by elementary analysis. We, therefore, arrived at the conclusion that Fischer's "benzimidazole-4,5-dicarboxylic anhydride" is nothing else than phthalimide. This conclusion was confirmed by the identity between the product of sublimation of the dicarboxylic acid obtained by oxidation of 1,2-naphthimidazole and commercial, chemically pure phthalimide.

It is impossible to visualize the formation of phthalimide from benzimidazole-4,5-dicarboxylic acid. Formation of phthalimide confirms the hypothesis that the product of oxidation of 1,2-naphthimidazole has the structure of o-carboxy-phenyl-imidazole-carboxylic acid (VI). Decomposition of the latter during sublimation results in formation also of other products among which could be detected hydrocyanic acid and carbon dioxide.

For final confirmation of the accuracy of our proposed scheme for the oxidation of 1,2-naphthimidazole and of the formula of the dicarboxylic acid, it was necessary also to isolate the intermediate product of this reaction — the quinone (VIII) which was not detected by Fischer.

After a number of experiments we succeeded in isolating and characterizing this substance. It forms orange-red crystals, soluble in glacial acetic acid, sulfuric acid and aqueous alkalies with a characteristic violet-red color. This compound gives a hydrazone and dihydrazone of the type of (IX,X), while with o-phenylenediamine and 1,2-naphthalenediamine it forms characteristic azines (XI,XII) - analogs of phenanthrazines.

We purified and analyzed all these derivatives. Further oxidation of the quihone gave the already described dicarboxylic acid (VI).



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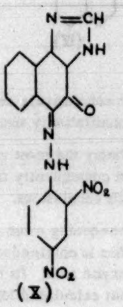

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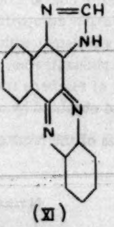
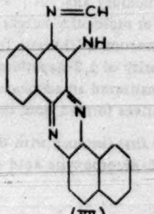


(XI)



(XII)

Consideration must also be given to the analogs of phenolphthalein and fluorescein mentioned by Fischer. Since o-carboxy-phenyl-imidazolecarboxylic acid was unstable, it might be suggested that these dyes are obtained from the products of their breakdown — phthalic acid — and are not analogs of phenolphthalein and fluorescein, as Fischer had thought, but these dyes themselves. Purification of the dyes obtained by interaction of the dicarboxylic acid (VI) with phenol in the first case and with resorcinol in the second case, and the identity of their absorption spectra with those of the commercial, chemically pure phenolphthalein and fluorescein respectively, confirmed this supposition.

EXPERIMENTAL

Preparation of 1,2-Naphthimidazole.

1,2-Naphthalenediamine was prepared by the known method [7].

Apart from the published methods of preparation [6,8], 1,2-naphthimidazole was synthesized mainly by our proposed method: 25.6 g 1,2-naphthalenediamine sulfate, 10 ml formic acid and 100 ml 10% hydrochloric acid were placed in a round-bottomed flask with a reflux condenser and boiled for 4 hours. After neutralization of the excess acid (violet stain on Congo paper) with aqueous ammonia, the solution was boiled with animal charcoal and filtered hot. The free base 1,2-naphthimidazole was separated from the cooled solution by addition of aqueous ammonia. The base was recrystallized from water or aqueous ethanol and dried at 90-100°; m.p. 174°; yield 14.95 g (89%).

Oxidation of 1,2-Naphthimidazole

1,2-Naphthimidazole was oxidized in a medium of glacial acetic acid with chromic oxide [6]. After recrystallization from water the oxidation product forms white, lustrous crystals melting at 251° and decomposing at 270°.

1,2-Naphthimidazole was also oxidized in sulfuric acid with sodium dichromate, and in this case the product of oxidation was purer and obtained in better yield.

16.8 g 1,2-naphthimidazole was dissolved in 150 ml sulfuric acid diluted with water in the ratio of 1:3. To this solution was gradually added a solution of chromic acid mixture (39.2 g $K_2Cr_2O_7$ in 200 ml 1:3 sulfuric acid) with constant stirring. Oxidation proceeded for 1.5 to 2 hours, after which the green solution was poured into three times the quantity of cold water; fine greenish-yellow crystals came down almost at once. These were filtered after cooling of the solution and washed with iced water until the green color of the wash water had disappeared. The acid was soluble in ethanol, glacial acetic acid and hot water, sparingly soluble in ether and ligroine. Purification was effected by reprecipitation with hydrochloric acid from alkaline solution and by recrystallization from water containing animal charcoal; m.p. 251°; yield 6.9 g (approx. 30%).

0.0986 g sub.: 0.2062 g CO_2; 0.0323 g H_2O. 0.1798 g sub.: 0.3741 g CO_2; 0.0542 g H_2O. 0.1069 g sub.: 11.7 ml N_2 (20°, 735.5 mm). 0.1130 g sub.: 12.3 ml N_2 (19°, 743 mm). Found %: C 57.07, 56.78; H 3.66, 3.37; N 12.23, 12.33. $C_9H_6O_4N_2$. Calculated %: C 52.43; H 2.94; N 13.59. $C_{11}H_8O_4N_2$. Calculated %: C 56.90; H 3.47; N 12.07.

Potentiometric titration of 0.1010 g substance: 8.7 ml 0.1 N NaOH. Found: M 234. $C_{11}H_8O_4N_2$. Calculated: M 232. $C_9H_6O_4N_2$. Calculated M 206.

The analytical results confirm the formula of the dicarboxylic acid (VI) which we advanced on the basis of the considerations set forth in the theoretical part.

Analysis of the silver salt:

1.0116 g sub.: 0.4875 g Ag. 0.3870 g sub.: 0.1877 g Ag. Found %: Ag 48.20, 48.50. $C_9H_4O_4N_2Ag_2$. Calculated %: Ag 51.38. $C_{11}H_6O_4N_2Ag_2$. Calculated %: Ag 48.43.

Dimethyl Ester of the Acid

1 g dicarboxylic acid was boiled for an hour in a solution of methanol (40 ml) with two parts KOH (0.4 g). After cooling, the solution was transferred to a tube to which was added 2 moles methyl iodide (1.42 g); the tube was sealed and heated for 3-4 hours in a gas furnace at 99-100°. After cooling and opening of the tube, the contents were transferred to a porcelain beaker and evaporated to dryness on a water bath. The residue was repeatedly and thoroughly washed with cold water, dried and twice recrystallized from ethanol; m.p. 130°. Yield 7.9 g (71%).

0.1093 g sub.: 0.2383 g CO_2; 0.0439 g H_2O. 0.1417 g sub.: 0.3093 g CO_2; 0.0596 g H_2O. 0.1055 g sub.: 10.1 ml N_2 (20°, 742 mm). 0.1242 g sub.: 12.2 ml N_2 (21°, 744 mm). Found %: C 59.5, 59.57; H 4.50, 4.71; N 10.90, 11.14. $C_{11}H_{10}O_4N_2$. Calculated %: C 56.40; H 4.23; N 12.00. $C_{13}H_{12}O_4N_2$. Calculated %: C 60.00; H 4.65; N 10.76.

Sublimation of the Dicarboxylic Acid

1) The recrystallized and dried substance was placed in a porcelain beaker, covered with an inverted funnel glass and slowly heated on a sand bath. The sublimed material collected on the sides of the funnel in the form of long, very faint-yellow needles with m.p. 225°.

2) Sublimation was effected in vacuum in a refractory flask with a broad tube, heated with an oil bath which enabled regulation of the temperature and avoided overheating of the substance.

0.1514 g sub.: 0.3612 g CO_2; 0.0471 g H_2O. 0.1101 g sub.: 0.2627 g CO_2; 0.0364 g H_2O. 0.1608 g sub.: 13.8 ml N_2 (21°, 740 mm). 0.1426 g sub.: 10.87 ml N_2 (22°, 738 mm). Found %: C 65.10, 65.08; H 3.40, 3.70; N 9.70, 9.66. $C_9H_4O_3N_2$. Calculated %: C 57.40; H 2.20; N 14.97. $C_8H_5O_2N$. Calculated %: C 65.30; H 3.40; N 9.51.

The product of sublimation crystallizes nicely from water and does not revert to the original acid during the process. After two recrystallizations from water it has m.p. 231° and mixed test with the unpurified substance gives m.p. 229°. The substance has good solubility in aqueous alkali and ammonia and remains unchanged when precipitated from an alkaline solution with acids in the cold. Liberation of ammonia was qualitatively observed when the product of sublimation was boiled in aqueous alkali.

A weighed sample of the product of sublimation was placed in a round-bottomed flask and dissolved in 40 ml 15% NaOH solution. The flask was provided with a trap for alkali spray, connected to a sloping water condenser and a receiver; into the flask, below the layer of alkali solution, was inserted a tube for introduction of steam. A standard 0.1N hydrochloric acid solution was placed in the receiver for trapping the ammonia which came off. Distillation was stopped when a drop of the distillate did not turn litmus paper blue. The contents of the receiver were titrated with 0.1 N NaOH solution in presence of methyl orange.

The results of the experiments are set forth in the Table.

Amount of 0.1 N HCl for taking-up of Ammonia = 40 ml

Weight of substance (in g)	Amount of NaOH used in titration (in ml)	N (in %)
0.3076	22.00	9.41
0.2692	24.15	9.65
0.3526	18.31	9.63
0.2962	20.10	9.50

The contents of the distillation flasks were combined, cooled and acidified with dilute hydrochloric acid until acid to Congo paper. Fine white crystals came down which after drying had m.p. 198°. The substance is readily soluble in water and ethanol, poorly in ether and chloroform; it crystallizes nicely from water. After purification, the m.p. is 203°. During the m.p. determination it was observed that if the melted substance was allowed to cool in the capillary and then melted again, it had m.p. 132°, not 203° as originally. The two compounds were identified as phthalic acid and phthalic anhydride. It was thus established that the investigated dicarboxylic acid was transformed into phthalimide during sublimation. After two recrystallizations the product of sublimation was identical in melting point with chemically pure, commercial phthalimide. The elementary analysis gave contents of carbon, hydrogen and nitrogen identical with those for phthalimide.

For the purpose of examination of the other products formed during sublimation of the dicarboxylic acid, the sublimation was effected in a quartz tube heated with a special small gas furnace provided with a thermometer. Sublimation was conducted in a stream of dry air free from carbon dioxide, and was continued for 3 hours. The following products were found as a result of decomposition of the dicarboxylic acid: carbon dioxide (from increase in weight of potash apparatus and from development of turbidity in barytes water) and hydrocyanic acid by qualitative reactions for the CN ion: 1) formation of Prussian blue (in a receiver with 0.1 N hydrochloric acid; 2) the characteristic odor of bitter almonds.

1,2-Imidazole-3,4-naphthoquinone

16.8 g naphthimidazole was dissolved in 150 ml glacial acetic acid or 96-98% acetic acid, heated to the boil, and addition was gradually made with constant stirring of a solution of 6.6 g chromic oxide in 50 ml acetic acid. Duration of oxidation 3-4 hours. The reaction product separated in part on pouring the reaction mass into water and in part after distillation of the acetic acid with steam from this solution. The orange-red crystals had m.p. 318-320° (at 300° the substance darkens and melts unsharply, with decomposition); the product is poorly soluble in cold water, slightly soluble in ethanol, and nearly insoluble in ether and benzene. It dissolves very well in aqueous solutions of alkalies with an intense violet-red color, rather less readily and with a less intense color in aqueous ammonia; on acidification of the alkaline solution it comes down again; it is easily reduced by sodium hydrosulfite in an alkaline medium. The substance was purified by recrystallization from nitrobenzene, washing with ether, and recrystallization from water. Yield 6.6 g (34%).

0.1018 g sub.: 0.2480 g CO_2; 0.0272 g H_2O. 0.0967 g sub.: 0.2350 g CO_2; 0.0275 g H_2O. 0.1235 g sub.: 15.4 ml N_2 (18°, 738 mm). 0.1109 g sub.: 14.01 ml N_2 (20°, 742 mm). Found %: C 66.51, 66.34; H 2.99, 3.18; N 14.2, 14.37. $C_{11}H_6O_2N_2$. Calculated %: C 66.7; H 3.05; N 14.14.

Synthesis of Derivatives of the Quinone

1) 0.5 g quinone was dissolved in the smallest possible amount of ethanol, and to this solution was added excess of phenylhydrazine solution (2 g of the hydrochloride and 3 g sodium acetate in 20 ml water). The solution was refluxed in a flask on a water bath for about a half hour, during which period attractive red crystals of the osazone began to separate in quantity which increased with progressive cooling of the solution. The substance was filtered off and purified by recrystallization from anhydrous ethanol. M.p. above 350°.

0.1073 g sub.: 0.2655 g CO_2; 0.0444 g H_2O. 0.1214 g sub.: 0.3235 g CO_2: 0.0531 g H_2O. 0.0981 g sub.: 19.2 ml N_2 (21°, 738 mm). Found %. C 72.60, 72.71; H 4.63, 4.90; N 22.12. $C_{23}H_{18}N_6$. Calculated %: C 73.04; H 4.76; N 22.20.

2) 2.6 g quinone and 1.53 g p-nitrophenylhydrazine were dissolved in glacial acetic acid and the solution refluxed in a flask for 20-30 minutes. On cooling the hydrazone crystallizes in the form of fairly large red crystals which were filtered and recrystallized from glacial acetic acid. M.p. above 350°.

0.1036 g sub.: 20.4 ml N_2 (20°, 742 mm). 0.0975 g sub.: 19.3 ml N_2 (21°, 740 mm). 0.1106 g sub.: 0.2428 g CO_2; 0.0375 g H_2O. 0.1094 g sub.: 0.2473 g CO_2; 0.0385 g H_2O. Found %. C 59.93, 61.67; H 3.80, 3.94; N 22.42, 22.41. $C_{17}H_{11}O_3N_5$. Calculated %: C 61.30; H 3.76; N 22.10.

3) 2 g dinitrophenylhydrazine was dissolved in 4 ml warm conc. sulfuric acid and diluted with 25 ml anhydrous ethanol. A solution of 2.6 g of the quinone in methanol was added in one portion to this solution, and the mixture was refluxed for a short time in a flask. Red crystals of the hydrazone separated even from the hot solution; after cooling they were filtered, washed with a small quantity of anhydrous ethanol and recrystallized from nitrobenzene. M.p. above 350°.

0.1011 g sub.: 0.1988 g CO_2; 0.0251 g H_2O. 0.1024 g sub.: 20.0 ml N_2 (22°, 742 mm). Found %: C 53.67; H 2.78; N 22.06. $C_{17}H_{10}O_5N_6$. Calculated %: C 54.00; H 2.69; N 22.20.

4) 2.6 g quinone was dissolved in boiling water and into this solution was run a boiling aqueous solution of 1.08 g o-phenylenediamine. Heating was continued for about 3 hours until separation of the yellow precipitate of the azine (XI) had ceased. Yield 2.16 g (78%).

0.1716 g sub.: 0.4720 g CO_2; 0.0558 g H_2O. 0.1207 g sub.: 22.5 ml N_2 (20°, 736 mm) 0.0851 g sub.: 15.9 ml N_2 (21°, 734 mm). Found %. C 75.08; H 3.64; N 21.02, 20.97. $C_{17}H_{10}N_4$. Calculated %: C 75.30; H 3.57; N 20.73.

5) 2.6 g quinone was condensed with 1.58 g 1,2-napthrhalenediamine as in the preceding case. Yield of azine (XII) 2.3 g (72%). Melting point of both azines above 350°.

0.1142 g sub.: 0.3284 g CO_2; 0.0390 g H_2O. 0.0915 g sub.: 14.47 ml N_2 (22°, 740). Found %: C 78.47; H 3.91; N 17.83. $C_{21}H_{12}N_4$. Calculated %: C 78.75; H 3.75; N 17.50.

Oxidation of the Quinone

5 g quinone was dissolved in 75 ml sulfuric acid (1:3) and to this solution was gradually added 6 g potassium bichromate. Oxidation was continued for 50-60 minutes, after which the reaction mass was poured into water; 6-8 hours later the small amount of substance was filtered off and after recrystallization from water and drying it had m.p. 251° and was identified as 5-phenylimidazole-3,4-dicarboxylic acid. Yield 0.43 g (approx. 8%).

SUMMARY

1. Further consideration of the previously developed concepts of the influence of the imidazole ring on the benzene ring condensed with it points to chemical similarity between 1,2-naphthimidazole and phenanthrene.

2. An experimental study of the oxidation of 1,2-naphthimidazole confirms this conclusion. This study shows that the reaction at first leads to formation of 1,2-naphthimidazole-3,4-quinone, which further oxidizes to phenylimidazole-dicarboxylic acid. The latter was erroneously assumed by Fischer to be 3,4-benzimidazole-dicarboxylic acid.

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REACTION OF NITROSTYRENE WITH SOME COMPOUNDS CONTAINING METHYLENE GROUPS ACTIVATED BY CARBONYL AND CARBOXYL GROUPS

V.V. Perekalin and A.S. Sopova

We have studied the interaction of β-nitrostyrene with substances containing labile hydrogen atoms in the methylene and methyl groups.

The hydrogen atoms were activated by electronophilic groups (carboxyl, carbonyl, cyano, and also by the nitrogen atoms of heterocycles) located in the alpha-position to, or conjugated with, methylene and methyl groups.

Literature data about the reaction of nitroolefins with compounds containing active methyl and methylene groups are scanty [1-3];

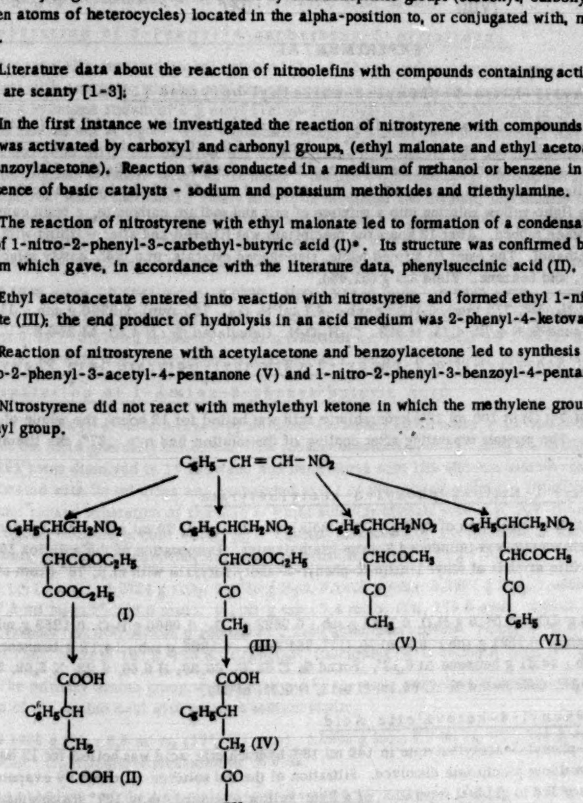
In the first instance we investigated the reaction of nitrostyrene with compounds in which the methylene group was activated by carboxyl and carbonyl groups, (ethyl malonate and ethyl acetoacetate, acetylacetone and benzoylacetone). Reaction was conducted in a medium of methanol or benzene in the cold and with heating in presence of basic catalysts - sodium and potassium methoxides and triethylamine.

The reaction of nitrostyrene with ethyl malonate led to formation of a condensation product - the ethyl ester of 1-nitro-2-phenyl-3-carbethyl-butyric acid (I)*. Its structure was confirmed by hydrolysis in an acid medium which gave, in accordance with the literature data, phenylsuccinic acid (II).

Ethyl acetoacetate entered into reaction with nitrostyrene and formed ethyl 1-nitro-2-phenyl-3-acetyl-butyrate (III); the end product of hydrolysis in an acid medium was 2-phenyl-4-ketovaleric acid (IV).

Reaction of nitrostyrene with acetylacetone and benzoylacetone led to synthesis of two condensation products: 1-nitro-2-phenyl-3-acetyl-4-pentanone (V) and 1-nitro-2-phenyl-3-benzoyl-4-pentanone (VI).

Nitrostyrene did not react with methylethyl ketone in which the methylene group was activated only by one carbonyl group.



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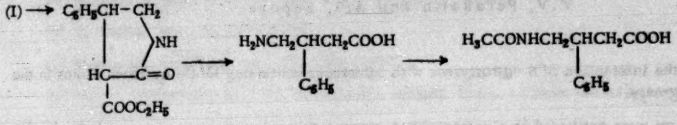
* In the nomenclature common outside Russia this acid might be named: α-carb-ethyl-β-phenyl-γ-nitrobutyric acid. Similar consideration apply to other compounds in this paper. Publisher.

Only a few methods of synthesis of γ-aminobutyric acid are known [4]; reactions leading to formation of its derivatives are even less developed [5]; special attention was, therefore, given to investigation of the transformations of the product of condensation of nitrostyrene with ethyl malonate with the aim of synthesizing derivatives of γ-amino acids. Reduction of (I) with hydrogen in presence of nickel catalyst led to a nearly quantitative yield of 3-phenyl-4-carbethoxy-5-pyrrolidone (VII), prolonged heating of which with 20% hydrochloric acid transformed it into 1-amino-2-phenyl-butyric acid (VIII) (75.6%). This amino acid, in contrast to the lactam (VII), readily and quantitatively gives the reaction for a primary amino group with nitrous acid, and when heated with acetic anhydride it formed 1-acetylamino-2-phenyl-butyric acid (IX) (yield 76.4%).



(VII) (VIII) (IX)

EXPERIMENTAL

1. Preparation of Ethyl 1-Nitro-2-phenyl-3-carbethyl-butyrate [1]

To a solution of sodium ethyl malonate, prepared by adding 1 g sodium to a mixture of 7.2 g (0.045 mole) ethyl malonate in 50 ml dry methanol, was added at 10-15° a solution of 5.2 g (0.035 mole) β-nitrostyrene in 50 ml dry methanol; the mixture was heated in the absence of moisture for 2 hours at 50-55°. After cooling, the red solution was neutralized with 100% acetic acid and then saturated at 0-5° with dry hydrogen chloride until acidic; on pouring the light-yellow solution into a mixture of salt and sodium carbonate, a resin came down which gradually solidified when rubbed. After 12 hours the precipitate was filtered and after washing with water it was crystallized from methanol. The ester (I) formed white, star-shaped crystals, m.p. 64°, easily soluble in methanol, ethanol, acetone, and benzene. Yield 5.5 g (51.4%).

0.1023 g sub.: 6.8 ml N_2 (18°, 770 mm). 0.1160 g sub.: 4.7 ml N_2 (14°, 750 mm). 0.2200 g sub.: 11.96 g benzene: Δt 0.31°. Found %: N 4.72, 4.73; M 303. $C_{15}H_{19}O_6N$. Calculated %: N 4.53; M 309.2.

2. Transformation of Ethyl 1-Nitro-2-phenyl-3-carbethyl-butyrate into Phenylsuccinic Acid

A weighed amount of 1 g (I) in 100 ml 18% hydrochloric acid was boiled for 12 hours; the whole of the solid gradually went into solution. The crystals separating after cooling of the solution had m.p. 167°; the literature [6] gives m.p. 167°.

3. Preparation of Ethyl 1-Nitro-2-phenyl-3-acetylbutyrate

Into a mixture consisting of a solution of 2.08 g (0.014 mole) nitrostyrene in 20 ml anhydrous benzene and 2.6 g (0.020 mole) ethylacetoacetate was introduced 3 drops triethylamine. Evaporation of the solution 10 hours later caused separation of white crystals of ethyl 1-nitro-2-phenyl-3-acetylbutyrate with m.p. 76° (from ethanol). Yield 3.8 g (98%).

0.1134 g sub.: 0.2512 g CO_2; 0.0615 g H_2O. 0.1185 g sub.: 0.2622 g CO_2; 0.0660 g H_2O. 0.1253 g sub.: 5.3 ml N_2 (14°, 776 mm). 0.1521 g sub.: 6.6 ml N_2 (17°, 761 mm). 0.1665 g sub.: 14.19 g benzene Δt 0.22°. 0.1094 g sub.: 14.81 g benzene Δt 0.13°. Found %: C 60.45, 60.38; H 6.06, 6.23; N 5.09, 5.07; M 272, 275. $C_{14}H_{17}O_5N$. Calculated %: C 60.18; H 6.13; N 5.01; M 279.

4. Preparation of 2-Phenyl-4-ketovaleric Acid

1.4 g ethyl 1-nitro-2-phenyl-3-acetylbutyrate in 140 ml 18% hydrochloric acid was boiled for 12 hours; gradually the whole of the resinous precipitate dissolved. Filtration of the red solution followed by evaporation to 1/10 of its original volume led to gradual separation of a light-yellow substance, m.p. 127° (from ethanol); the literature reports m.p. 127° [7].

5. Preparation of 1-Nitro-2-phenyl-3-acetyl-4-pentanone

To a mixture consisting of a solution of 1.5 g (0.01 mole) nitrostyrene in 15 ml anhydrous benzene and 1.2 g (0.012 mole) acetylacetone was added 3 drops triethylamine. After 10 hours the solution was evaporated and yielded acicular crystals of 1-nitro-2-phenyl-3-acetyl-4-pentanone with m.p. 114° (from ethanol). Yield 2 g (77.7%).

0.1139 g sub.: 0.2606 g CO_2; 0.0685 g H_2O. 0.1294 g sub.: 6.6 ml N_2 (17°, 752 mm). 0.1136 g sub.: 5.7 ml N_2 (16°, 765 mm). Found %: C 62.43; H 6.72; N 5.89, 5.92. 0.1011 g sub.; 14.24 g benzene: Δt 0.15°. 0.1981 g sub.; 14.24 g benzene: Δt 0.28°; M 241, 253. $C_{13}H_{15}O_4N$. Calculated %: C 62.61; H 6.69; N 5.62; M 249.

6. Preparation of 1-Nitro-2-phenyl-3-benzoyl-4-pentanone

To a mixture prepared by mixing a solution of 1.5 g (0.01 mole) nitrostyrene in 15 ml anhydrous benzene with 1.62 g (0.01 mole) benzoylacetone in 10 ml anhydrous benzene was added 3 drops triethylamine. Evaporation of the solution after 10 hours gave a resinous mass which after trituration with ethanol changed into white crystals.

1-Nitro-2-phenyl-3-benzoyl-4-pentanone had m.p. 131° (from ethanol). Yield 2.7 g (86%).

0.1132 g sub.: 0.2875 g CO_2; 0.0580 g H_2O. 0.1039 g sub.: 0.2638 g CO_2; 0.0528 g H_2O. 0.1080 g sub.: 4.3 ml N_2 (23°, 769 mm). 0.1153 g sub.: 4.6 ml N_2 (20°, 759 mm). 0.1037 g sub.; 14.10 g benzene Δt 0.13°. 0.2194 g substance: 14.10 g benzene: Δt 0.26°. Found %: H 5.73, 5.68; N 4.60, 4.60; M 288, 303. $C_{18}H_{17}O_4N$. Calculated %: C 69.42; H 5.57; N 4.50; M 311.

7. Preparation of 3-Phenyl-4-carbethoxy-5-pyrrolidone

5 g specially prepared nickel catalyst [8] and 70 ml methanol were saturated with hydrogen in the course of 2 hours with energetic stirring until the gas ceased to be absorbed at room temperature. Addition was then made in a hydrogen stream of 5 g ethyl 1-nitro-2-phenyl-3-carbethyl-butyrate in 10 ml methanol. Hydrogenation was carried out at 30-40° with vigorous shaking; in 5 hours 1000 ml hydrogen was absorbed (the calculated amount was 1050 ml). The catalyst was then removed by filtration and the alcoholic filtrate evaporated to 0.1 of its original volume. After 12-14 hours 3-phenyl-4-carbethoxy-5-pyrrolidone separated (white crystals) with m.p. 132° (from methanol), easily soluble in methanol and ethanol, less readily in water; stable to heating in water (no change when heated for 2 hours at 180-190°). A positive reaction for a primary amino group (nitrogen liberation) occurs when an aqueous solution of the substance and sodium nitrite is treated with a two-fold excess of hydrochloric acid on a boiling water bath (the reaction does not go in the cold). Yield 3.53 g (97%).

0.1243 g sub.: 0.3044 g CO_2; 0.0720 g H_2O. 0.1149 g sub.: 0.2813 g CO_2; 0.0680 g H_2O. 0.1107 g sub.: 6.2 ml N_2 (19°, 742.5 mm). 0.1273 g sub.: 6.7 ml N_2 (18°, 767.5 mm). 0.1553 g sub.: 13.31 g benzene: Δt 0.27°. 0.2784 g substance; 13.31 g benzene: Δt 0.46°. Found %: C 66.82, 66.81; H 6.48, 6.62. N 6.34, 6.18; M 220, 231. $C_{13}H_{15}O_3N$. Calculated %: C 66.91; H 6.48; M 233.

8. Preparation of 1-Amino-2-phenyl-butyric Acid

3 g 3-phenyl-4-carbethoxy-5-pyrrolidone was boiled for 16 hours in 300 ml 18% hydrochloric acid; the whole of the solid gradually dissolved. The product obtained by evaporating the solution on a water bath (m.p. 195°) was dissolved in 10 ml water and neutralized with 10% aqueous sodium carbonate. The solution was twice treated with 25 ml ether and evaporated to 0.1 of the original volume. Dilution with double the amount of ethanol caused separation of the acid as white acicular crystals with m.p. 209° (from aqueous ethanol). The acid is readily soluble in cold water, pH of aqueous solution 6.5; it is insoluble in methanol, ethanol, acetone, chloroform, carbon tetrachloride, benzene and pyridine. Yield 1.74 g (75.6%).

0.1111 g sub.. 0.2724 g CO_2; 0.0750 g H_2O. 0.1428 g sub.: 0.3521 g CO_2; 0.0966 g H_2O. 0.1091 g sub.: 7.3 ml N_2 (17°, 768.5 mm). 0.1121 g sub.: 7.4 ml N_2 (17°, 770.5 mm). 0.0103 g sub.: 0.1069 g camphor Δt 23°. 0.0101 g substance; 0.1050 g camphor: Δt 22°. Found %: C 66.9, 67.28; H 7.55, 7.51; N 7.90, 7.82; M 167.5, 174.8. $C_{10}H_{13}O_2N$. Calculated %: C 66.99; H 7.31; N 7.82; M 179.

The primary amino group was determined by the usual procedure of acting on a hydrochloric acid solution of the amino acid with aqueous sodium nitrite.

0.1000 g sub.: 6.8 ml N_2 (17°, 761 mm). 0.0900 g sub.: 6.2 ml N_2 (17°, 765.5 mm). Found %: N 7.95, 8.10. $C_{10}H_{13}O_2N$. Calculated %: N 7.82.

9. Preparation of 1-Acetylamino-2-phenyl-butyric Acid

1.5 g 1-amino-2-phenyl-butyric acid and 15 ml acetic anhydride were boiled for 3 hours; after cooling, the solution was filtered and neutralized with 10% aqueous sodium carbonate to bring down a precipitate of 1-acetylamino-2-phenyl-butyric acid in the form of lustrous lozenges with m.p. 65° (from n-hexane). The substance is insoluble in water, soluble in methanol, ethanol, acetone, chloroform, and n-hexane. Yield 1.4 g (76.4%).

0.0916 g sub.: 5.2 ml N_2 (16°, 752 mm). Found %: N 6.59. $C_{12}H_{15}O_3N$. Calculated %: N 6.33.

SUMMARY

1. It is shown that nitrostyrene reacts in presence of basic catalysts with various compounds containing methylene groups activated by carbonyl and carboxyl groups.

2. A new method of synthesis of derivatives of γ-amino acids is proposed.

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* This patent no. and year are as given in the original journal. Publisher.

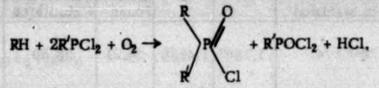
SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS FROM HYDROCARBONS AND THEIR DERIVATIVES

IV. FORMATION OF DERIVATIVES OF DIALKYLPHOSPHINIC ACIDS FROM ALKYLDICHLOROPHOSPHINES, HYDROCARBONS AND OXYGEN

L.Z. Soborovsky and Yu. M. Zinovyev

We previously effected reactions of phosphorus trichloride and oxygen with paraffinic, olefinic and acetylenic hydrocarbons and some of their derviatives [1,2,3]. It was considered expedient to investigate the possibility of formation of a phosphorus-carbon linkage in the conditions of the described process when phosphorus trichloride was replaced by certain other compounds containing phosphorus in the trivalent state. As compounds of this type we selected alkyldichlorophosphines, since in their case we should expect formation of derivatives of secondary (including mixed) dialkylphosphinic acids. As we know, the starting dialkylchlorophosphines, as well as the aryldichlorophosphines, have become relatively accessible compounds as a result of recently published researches [4,5].

The experimental work confirmed the above suggestion: on passing oxygen through a mixture of methyl- or ethyldichlorophosphine and propane, cyclohexane or allyl chloride, the chlorides of the corresponding secondary phosphinic acids were obtained, i.e. the chlorides of methylpropyl-, methylcyclohexyl-, ethylcyclohexyl- and ethyldichloropropylphosphinic acids. At the same time methyl- or ethyldichlorophosphine were formed as products of direct oxidation, i.e. the acid chlorides of methane- or ethanephosphinic acid:



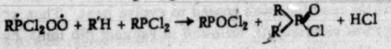
$$RH + 2R'PCl_2 + O_2 \rightarrow R_2P(O)Cl + R'POCl_2 + HCl.$$

The application in this reaction of compounds so diverse in character as propane, cyclohexane and allyl chloride demonstrates that the reaction of alkyldichlorophosphines with oxygen and aliphatic hydrocarbons can be extended to a great number of diverse compounds of the paraffinic, olefinic and, apparently, acetylenic series.

In the reaction considered, just as in those previously described, the main process is the oxidation of the initial trivalent phosphorus compound. A large proportion of the alkyldichlorophosphines is thereby transformed into alkanephosphinyl chlorides. These chlorides are formed in a yield of 20-25% reckoned on the reacted alkyldichlorophosphine. Thus, for example, on reaction with allyl chloride, 58% of the initial ethyldichlorophosphine was transformed into ethyldichloroxyphosphine and only 14% into ethyldichloropropylphosphinyl chloride.

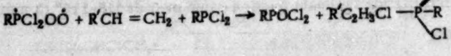
The mechanism of the reaction in question may be represented by the following scheme, in analogy with that previously described [2]:

$$R\dot{P}Cl_2 + O_2 \rightarrow R\dot{P}Cl_2O\dot{O}$$



$$R\dot{P}Cl_2O\dot{O} + R'H + RPCl_2 \rightarrow RPOCl_2 + RR'P(O)Cl + HCl$$

or (in the case of unsaturated compounds):



$$R\dot{P}Cl_2O\dot{O} + R'CH=CH_2 + RPCl_2 \rightarrow RPOCl_2 + R'C_2H_3Cl-P(O)(R)Cl$$

EXPERIMENTAL

Preparation of Methylpropylphosphinyl Chloride (I)

In a reactor, fitted with a gas-leading tube, was placed 114 g methyldichlorophosphine (0.974 mole). The reactor was cooled in a mixture of carbon dioxide and acetone, and 97 g propane (1.975 mole) was condensed in it. Through the mixture at -60° was passed oxygen. The evolved gases passed through a carbon dioxide trap and then into the fume cupboard. The propane condensing in the trap was returned to the reactor. Passage of oxygen was continued until the reaction mass in the reactor had changed into a crystalline mass. The temperature in the reactor was gradually raised and at the end of the experiment was -5°. For removal of low-boiling reaction products, the mass was heated on a bath to 140°, at first at atmospheric pressure and later at 25 mm. The residue after distillation of the methyldichloroxyphosphine was distilled at 73-85° (3-4 mm). 16.9 g substance came over On redistillation the main mass of substance boiled at 78-81° (4 mm); d_4^{20} 1.1307; n_D^{20} 1.4628.

3.790 mg sub.: 4.620 mg CO_2; 2.920 mg H_2O. 4.440 mg sub.: 5.450 mg CO_2; 2.785 mg H_2O. 0.1547 g sub.: 11.11 ml 0.1 N $AgNO_3$. 0.1118 g substance: 8.06 ml 0.1 N $AgNO_3$. 4.525 mg substance: 69.460 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 8.690 mg substance: 133.800 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 0.4408 g substance: 12.55 ml 0.5 N NaOH. Found %: C 33.55, 33.50; H 6.92, 7.01; Cl 25.50, 25.6; P 22.32, 22.39; equiv. 2.025. $C_4H_{10}OClP$. Calculated %: C 34.17; H 7.17; Cl 25.22; P 22.03; equiv. 2.00.

Preparation of Methylcyclohexylphosphinyl Chloride (II)

A stream of oxygen from a cylinder was passed for 5 hours through a mixture of 51 g cyclohexane and 136 g methyldichlorophosphine at 20-25°. The low boiling substances (unreacted cyclohexane and methyldichlorophosphine) were then distilled off from the reaction mixture at atmospheric pressure, and 21 g cyclohexane was collected. After removal of the methyldichlorophosphine (at 20 mm), the residue came over at 110-128° (2 mm). Yield 28.6 g. On redistillation the substance boiled at 101-102° (3 mm), and solidified at 26°; d_4^{20} 1.1611; n_D^{20} 1.4988.

0.2226 g sub.: 12.33 ml 0.1 N $AgNO_3$. 0.2243 g sub.: 12.55 ml 0.1 N $AgNO_3$. 6.370 mg sub.: 74.830 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. 6.500 mg substance: 74.460 mg $(NH_4)_3PO_4 \cdot 12MoO_3$. Found %: Cl 19.65, 19.87; P 16.62, 16.66. $C_7H_{14}OClP$. Calculated %: Cl 19.63; P 17.15.

Properties of Synthesized Substances

No. of compound	Formulas of synthesized compounds	M.p.	B.p. (pressures in mm in brackets)	d_4^{20}	n_D^{20}	MR_D		Yield in % of hydrocarbon consumed)
						Found	Calculated	
(I)	CH_3 $\rangle POCl$ C_3H_7	-	78-81° (4)	1.1307	1.4628	34.21	33.50	25
(II)	CH_3 $\rangle POCl$ C_6H_{11}	26	101–102 (3)	1.1611	1.4988	45.65	45.14	44
(III)	C_2H_5 $\rangle POCl$ C_6H_{11}	-	118 (3)	1.1372	1.5002	50.35	49.76	68
(IV)	C_2H_5 $\rangle POCl$ $C_3H_5Cl_2$	-	115–120 (2)	1.3492	1.4980	48.55	47.84	47
(V)	$C_2H_5POCl_2$*	-	45–46 (3)	1.3678	1.4661	29.80	29.49	58 (on amount taken in the reaction)

Preparation of Ethylcyclohexylphosphinyl Chloride (III)

Dry oxygen was passed through a mixture of 84.5 g (0.645 mole) ethyldichlorophosphine and 27.2 g (0.324 mole) cyclohexane until the reaction mass ceased to evolve heat. Then at atmospheric pressure the unreacted cyclohexane (22.2 g) was distilled off, followed in vacuum (20 mm) by the ethyldichlorophosphine and ethyldichloroxyphosphine. The residue was distilled at 110-130° (4 mm). Yield 68 % calculated on the cyclohexane consumed. On redistillation the main fraction came over at 118-119° (3 mm).

d_4^{20} 1.1372; n_D^{20} 1.5002.

3.681 mg sub.: 6.600 mg CO_2; 2.720 mg H_2O. 4.352 mg sub.: 7.775 mg CO_2; 3.335 mg H_2O. 0.2101 g sub.: 10.7 ml 0.1 N $AgNO_3$. 0.1978 g sub.: 10.2 ml 0.1 N $AgNO_3$. Found %: C 48.93, 48.58; H 8.26, 8.60; Cl 18.04, 18.29. $C_8H_{16}OClP$. Calculated %: C 49.34; H 8.29; Cl 18.23.

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* The compound was first prepared by Michaelis [6] and characterized by Guichard [7]. The latter erroneously attributes to ethyldichlorophosphine d_4^{20} 1.1883.

Preparation of Ethyldichloropropylphosphinyl Chloride (IV)*

Dry oxygen was passed through a mixture of 54.8 g (0.418 mole) ethyldichlorophosphine and 34.6 g (0.452 mole) allyl chloride until heat evolution by the reaction mass had ceased. From the reaction mass was distilled 18.6 g unreacted allyl chloride, 35.8 g ethanephosphinyl chloride, and 16.5 g of a high-boiling product which came over up to 120° (3 mm). Redistillation gave a 115-120° (2 mm) fraction; d_4^{20} 1.3492; n_D^{20} 1.4980. Yield 47% reckoned on the allyl chloride consumed.

3.875 mg sub.: 3.790 mg CO_2; 1.810 mg H_2O. 4.225 mg sub.: 4.200 mg CO_2; 2.165 mg H_2O. 0.1436 g sub.: 6.53 ml 0.1 N $AgNO_3$. 0.0668 g sub.: 3.05 ml 0.1 N $AgNO_3$. Found %: C 26.69, 27.12; H 5.23, 5.73; Cl** 16.13, 16.21. $C_5H_{10}OCl_3P$. Calculated %: C 26.90; H 4.51; Cl** 15.86.

SUMMARY

1. It is shown that a C–P bond is formed on interaction of hydrocarbons of the aliphatic series or their chloro derivatives with oxygen and alkyldichlorophosphines.

2. Chlorides of secondary (mixed) dialkylphosphinic acids were prepared. The reaction was effected between methyl- or ethyldichlorophosphines and propane, cyclohexane or allyl chloride.

3. The chlorides of methylpropyl-, methylcyclohexyl-, ethylcyclohexyl- and ethyldichloropropylphosphinic acids were synthesized.

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* See Consultants Bureau Translation, p. 391.

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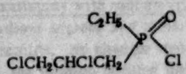
* The compound is apparently a mixture of the isomers



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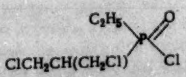


The question of the position of the chlorine atoms in the hydrocarbon radical of the compound prepared is not considered in the present communication.

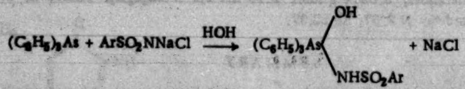
** Identified as hydrolyzable chlorine.

REACTION OF TRIPHENYLANTIMONY WITH THE SODIUM SALT OF N-BROMOACETAMIDE

L.P. Petrenko

Representatives of organometallic compounds of elements of the fifth group of Mendeleev's periodic system with salts of N-chloroamides which have been studied are organoarsenic and organophosphorus compounds [1,2,3]. A general feature of this reaction is that, depending on the reaction conditions, formation occurs of arsine oxides or of hydroxy derivatives of arsineimines when the reaction takes place in presence of moisture:

$$(C_6H_5)_3As + ArSO_2NNaCl \xrightarrow{HOH} (C_6H_5)_3AsO + ArSO_2NH_2 + NaCl$$



$$(C_6H_5)_3As + ArSO_2NNaCl \xrightarrow{HOH} (C_6H_5)_3As\left<\begin{matrix}OH\\NHSO_2Ar\end{matrix}\right. + NaCl$$

On carrying out the reaction in the absence of moisture, however, there is a quantitative yield of arsineimines:

$$(C_6H_5)_3As + ArSO_2NNaCl \longrightarrow NaCl + (C_6H_5)_3AsNSO_2Ar.$$

Tertiary phosphines react in exactly the same manner with N-chloroamides. Nothing has been published in the literature about the reactions of organoantimony compounds with salts of N-chloroamides.

Since phosphorus, arsenic and antimony occur in the same group of the periodic system and since organophosphorus and organoantimony compounds react with sodium salts of N-chloroamides when simply brought together both in solvents and without solvents, we inferred that triphenylantimony would also react with sodium salt of N-bromoacetamide with formation of the stibineimine. The experimental work on these lines did not confirm our predictions although the reactions were performed in a variety of conditions (duration, temperature, solvents, and ratios of reactants). Only the addition of a small amount of conc. hydrochloric acid as catalyst gave the opportunity of obtaining the condensation product – triphenylantimonyacetimine:

$$(C_6H_5)_3Sb + CH_3CONNaBr \longrightarrow NaBr + (C_6H_5)_3SbNCOCH_3.$$

The composition of triphenylantimonyacetimine was confirmed both by quantitative analysis for antimony and nitrogen and by formation of derivatives with copper chloride and mercury chloride. Analysis established that one mole of triphenylantimonyacetimine reacts with one mole of copper chloride or mercury chloride.

EXPERIMENTAL

The triphenylantimony required for the investigations was synthesized from antimony trichloride, bromobenzene and magnesium powder in a medium of anhydrous ether [4]. After purification from diphenyl and other impurities by vacuum distillation, it formed white crystals with m.p. 49-50° and b.p. 220° at 12 mm.

The sodium salt of N-bromoacetamide was obtained by reacting acetamide with sodium hypobromide [5] followed by salting-out with acetone at a temperature of -10 to -15°; it formed white, hygroscopic crystals.

Found%: active Br 50.06, 49.55; N 8.52. $C_2H_3ONNaBr$. Calculated %: active Br 49.95; N 8.76.

Reaction of triphenylantimony with sodium salt of N-bromoacetamide. 3.5 g (0.01 mole) triphenylantimony was dissolved in 40 ml anhydrous acetone and to the solution in several portions was added 1.92 g (0.01 mole) sodium salt of N-bromoacetamide. No changes were observed. On adding 2-3 drops of conc. hydrochloric acid to the reaction mass, however, the solution became turbid and the temperature rose from 18 to 27°. The reaction was concluded by heating for another 30 minutes at 50° on a water bath; the precipitate, consisting of sodium bromide and unreacted sodium salt of N-bromoacetamide, was filtered off, and the mother liquor was evaporated in a vacuum at room temperature to a small volume. On cooling to -10°, the residual liquid in the flask crystallized. The crystals were filtered off, washed with anhydrous ether and dried in a desiccator. After recrystallization from anhydrous ether, triphenylantimonyacetimine had m.p. 157-159°. Yield 3.06 g or 74.63% of the theoretical. The white crystalline compound has good solubility in chloroform, acetone and benzene; it is sparingly soluble in ether and ethanol, insoluble in water. The pH of the aqueous ethanolic solution at the quinhydrone electrode was 6.1.

0.0684 g sub.: 1.53 ml 0.1 N H_2SO_4. 0.0720 g sub.: 3.5 ml 0.1 N $Na_2S_2O_3$. Found %: N 3.12; Sb 29.59. $C_{20}H_{18}ONSb$. Calculated %: N 3.42; Sb 26.69.

Derivatives of triphenylantimonyacetimine with mercury chloride and copper chloride were prepared for confirmation of the structure.

0.35 g triphenylantimonyacetimine was dissolved in 5 ml chloroform, and into the solution was run 5 ml 5% solution of mercuric chloride in ethanol. After 24 hours 0.3 g white rhombie crystals separated out; m.p. 126-128°, readily soluble in chloroform, acetone and carbon tetrachloride; insoluble in water.

0.0428 g sub.: 0.635 ml 0.1 N H_2SO_4. 0.0312 g sub.: 0.897 ml 0.1 N $Na_2S_2O_3$. Found %: N 2.08; Sb 17.59. $C_{20}H_{18}ONSbHgCl_2$. Calculated %: N 2.05; Sb 17.89.

From 0.41 g triphenylantimonyacetimine dissolved in 5 ml chloroform and 2.56 ml 5% copper chloride solution was obtained 0.35 g white lamellar crystals which were washed with water and dried over calcium chloride in a desiccator. M.p. 138-140°. Readily soluble in chloroform, acetone, ethanol and carbon tetrachloride; insoluble in water.

0.0646 g sub.: 1.14 ml 0.1 N H_2SO_4 0.0574 g sub.: 2.12 ml 0.1 N $Na_2S_2O_3$. Found %: N 2.47; Sb 22.47. $C_{20}H_{18}ONSbCuCl_2$. Calculated %: N 2.57; Sb 22.37.

SUMMARY

1. The reaction of triphenylantimony with the sodium salt of N-bromoacetamide was studied.

2. Triphenylantimony was synthesized for the first time and its properties were described.

3. The composition of triphenylantimonyacetimine was confirmed by formation of derivatives with mercuric chloride and cooper chloride.

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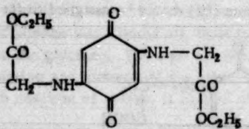
QUINONES

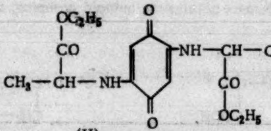
VI. CONDENSATION OF p-BENZOQUINONE WITH α-AMINO ACIDS

I.S. Ioffe and Z.Ya. Khavin

When quinones react with amino compounds, the amino nitrogen of the latter links up with carbon atoms of the quinone ring to form the corresponding derivatives of the mono- or diaminoquinone. Condensation products of this type were obtained by reacting quinones with various amines of both the aliphatic and aromatic series [1,2], including esters of α-amino acids [3,4]. Thus, for example, reaction of ethyl glycinate with p-benzoquinone gave the diester of diglycinoquinone (I), while the action of ethyl α-alaninate gave correspondingly the diester of dialaninoquinone (II) [3]:



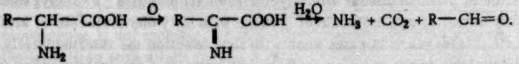
(I)



(II)

Analogous products of condensation of quinones with free α-amino acids, however, have not up to now been described.

It was established that reaction of quinones with α-amino acids yields the aldehydes corresponding to the latter with one carbon atom less, and that the reaction is accompanied by release of carbon dioxide and ammonia [5,6,7]; the quinone is at the same time changed into hydroquinone. The process is evidently one of oxidative cleavage of the α-amino acids due to the lability of the hydrogen atom at the α-carbon atom. The mechanism of oxidative cleavage of α-amino acids may be represented by the scheme:



$$R-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow{O} R-\underset{NH}{\underset{\|}{C}}-COOH \xrightarrow{H_2O} NH_3 + CO_2 + R-CH{=}O.$$

In the reaction of α-amino acids with quinones, however, the oxidative cleavage of the acids does not by any means proceed quantitatively, and is possibly accompanied by condensation of the acids with quinones by the mechanism usual for quinones of type (I).

Such a direction of the reaction was first suggested by Cooper [8,9] who studied the kinetics of reaction of p-benzoquinone and toluquinone with various α-amino acids in dilute aqueous solutions and observed that these solutions acquire a deep-red color. Cooper suggested that the bearer of this color was also the product of condensation of the quinone with the amino acid. He did not, however, isolate any such condensation products; nor was their separation described in later publications on the reaction of α-amino acids with quinones [10].

In our experiments we studied the reaction of p-benzoquinone with glycine and α-alanine, and for the first time we succeeded in isolating the condensation products.

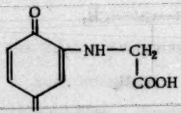
On pouring together heated aqueous solutions of quinone and glycine the reaction takes place with frothing due to oxidative cleavage of the amino acid, and an intense red color appears in the solution. At the same time, however, a dark-brown (nearly black) substance is precipitated whose quantity increases in the course of the reaction, and, especially when the temperature is raised, the red color of the solution disappears. This phenomenon alone prompted the idea that this red color, contrary to Cooper's suggestion, was not due to products of condensation of quinone with amino acid but to the presence of insignificant amounts of certain unstable substances, probably of a quinhydrone character. We obtained conclusive proof of the correctness of this theory by carrying out reactions relatively quickly at a low temperature in conditions facilitating development of the most intensive red color of the solution. On subsequently shaking the filtered aqueous solution with ether, the red color passed into the ethereal layer while the aqueous layer retained a brown color. From the aqueous layer, after evaporation and addition of ethanol, we isolated non-reacted glycine in the crystalline form. From the red ethereal solution, however, after drying and removal of the ether, we obtained a dry residue which only contained traces of nitrogen. This was identified as hydroquinone contaminated with insignificant amounts of colored impurities.

We found the product of condensation of p-benzoquinone with glycine in the precipitate resulting from heating of aqueous solutions of the starting components. The optimum yield was got by conducting the reaction at 50°.

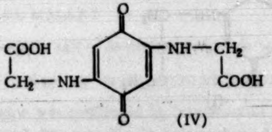
The substance formed is insoluble in water or ether. It is readily soluble in ethanol and acetic acid, but does not crystallize from these solvents. Dilution with water of the alcoholic or acetic acid solution of the substance precipitates it in the form of fine, dark-brown flocs. We used this method of purification of the substance.

The new compound is readily soluble in aqueous solutions of caustic alkalies or carbonates. Acidification of the alkaline solution brings down the substance in the form of fine, dark-brown flocs. Addition of hydrosulfite to the alkaline solution decolorizes it, but when the solution is then allowed to stand in contact with the air it again develops the brown color. This behavior points to the presence of a quinoid grouping in the compound. On dissolving the substance in an exactly calculated amount of water followed by addition of silver nitrate to the neutral solution, the water-insoluble silver salt comes down.

Quantitative determination of nitrogen in the thoroughly purified substance and of silver in the silver salt showed that the substance is the product of condensation of 1 molecule of p-benzoquinone with one molecule of glycine. Since the substance retains the quinoid grouping, the structure (III) should be assigned to it:



(III)



(IV)

When the reaction is carried out in the above-described optimum conditions, the yield of monoglycinoquinone (III) in relation to the glycine brought into reaction exceeds 50% of the theoretical. Bearing in mind that formation of glycinoquinone is also accompanied by oxidative cleavage of glycine, this yield must be regarded as fairly high.

In the reaction of p-benzoquinone with amino compounds the main product is usually, however, the diamino compound formed by introduction of two amino residues into the quinone molecule. Examples are the above-mentioned products of condensation of p-benzoquinone with glycine ester (I) and with α-alanyl ester (II). But the formation of products of condensation of one molecule of quinone with only one molecule of amino compound, similar to monoglycinoquinone (III), takes place in cases when with slow reaction the intermediately formed monoamino compound, which is insoluble in the reaction medium, separates as a precipitate, which is thereby removed from the sphere of the reaction. These conditions actually prevail during the interaction of p-benzoquinone with glycine in aqueous solution.

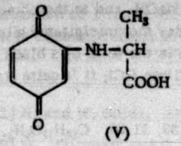
When the reaction is performed in ethanol, in which monoglycinoquinone (III) is soluble, the end product of reaction is diglycinoquinone (IV). Being poorly soluble in ethanol, diglycinoquinone is precipitated as formed, as a dark powder in a yield exceeding 30% in relation to the glycine brought into reaction.

Diglycinoquinone, like the monoglycino derivative, is soluble in aqueous alkalies and forms a stable, brown solution. Acidification of this solution brings down the diglycinoquinone unchanged. Addition to the sodium salt solution of silver nitrate brings down the water-insoluble silver salt.

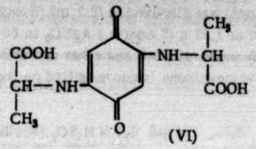
The composition of diglycinoquinone was confirmed by determination of the nitrogen content of the thoroughly purified product and of the silver content of its silver salt The structure of diglycinoquinone (IV) was confirmed by its preparation by saponification of the above-mentioned diethyl ester of diglycinoquinone (I), whose structure is not in doubt. Taking advantage of the relative stability of alkaline solutions of diglycinoquinone, we heated with 0.5 N sodium carbonate solution the ester of diglycinoquinone specially prepared from ethyl glycinate and quinone in accordance with the literature method [3]. The ester gradually went into solution, and acidification of the latter gave a diglycinoquinone identical in all its properties with the substance formed by reaction of p-benzoquinone with glycine in ethanolic solution.

Our experiments consequently showed that reaction of p-benzoquinone with glycine gives, apart from oxidative cleavage of the amino acid, products of condensation of the starting substances, monoglycinoquinone (III) and diglycinoquinone (IV).

Similarly in the reaction of p-benzoquinone with α-alanine there are formed, although in lower yields, monoalaninoquinone (V) in aqueous solution and dialaninoquinone (VI) in ethanolic solution.



(V)



(VI)

EXPERIMENTAL

I. Condensation of p-Benzoquinone with Glycine

Monoglycinoquinone

16.2 g benzoquinone (2 moles) was dissolved at 50° in 500 ml water. To this solution, with energetic stirring, was added dropwise a solution of 5.6 g glycine (1 mole) in 150 ml water at the same temperature. After the whole of the glycine solution had been added, the reaction mixture was stirred for 4 hours at 50° and then left overnight. By the next day it had completely lost its red color and had turned brown. The blackish-brown precipitate of monoglycinoquinone was filtered off, thoroughly washed with water, then with ether, and dried in the air. Yield 6.9 g (50.7% on the glycine). The aqueous mother liquor was shaken several times with ether; from the ethereal extract, after drying and removal of the ether, was obtained fairly pure hydroquinone; after two crystallizations from ether with addition of xylene, it melted at about 169°.

Monoglycinoquinone forms a black, friable powder. It is completely insoluble in cold water and nearly insoluble in hot; it is insoluble in ether, petroleum ether and ligroin. It is fairly easily soluble in ethanol and glacial acetic acid; dilution of the ethanolic or acetic acid solution with water precipitates it in the form of dark-brown flocs. On rapid heating in a capillary it melts with decomposition. It dissolves completely in dilute solution of sodium carbonate and sodium hydroxide, forming a brown solution of the sodium salt, from which it is again recovered by acidification with hydrochloric or sulfuric acid. If a weighed amount of monoglycinoquinone is exactly neutralized with a 2 N solution of NaOH (with transfer of a drop to phenolphthalein paper) and if silver nitrate solution is added to the obtained solution, the silver salt is formed. The latter forms a fine, very difficultly filterable, dark-brown precipitate; after thorough washing with water and drying at 60°, it forms a black powder with a metallic luster, completely insoluble in water.

Monoglycinoquinone is not modified by treatment with boiling dilute hydrochloric acid; it is also sufficiently stable to boiling with dilute caustic alkalies. Addition to the alkaline solution of monoglycinoquinone of sodium hydrosulfite with heating turns the solution light-yellow; on shaking in contact with the air it again oxidizes and darkens.

0.1278, 0.1628 g sub.: 6.69, 8.63 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 7.35, 7.42. $C_8H_7O_4N$. Calculated %: N 7.73.

A weighed sample of the silver salt was boiled in a Kjeldahl flask with 10 ml conc. HNO_3 (d 1.45) until completely decolorized. The AgCl was then precipitated as usual.

0.2241, 0.1944 g sub.: 0.1128, 0.0980 g AgCl. Found %: Ag 37.84, 37.96. $C_8H_6O_4NAg$. Calculated %: Ag 37.47.

Diglycinoquinone

8.1 g benzoquinone (3 moles) was dissolved in 200 ml ethanol. The solution was heated to 50° and addition was made, dropwise with energetic stirring, of a solution of 3.8 g glycine (2 moles) in 20 ml water. Heating was continued for 2 hours, after which the reaction mixture was left overnight. The next day, the black, easily filterable precipitate of diglycinoquinone was filtered from the brown ethanolic mother liquor, thoroughly washed with ethanol and ether, and dried in the air. Yield 2 g (31.3%). The ethanolic mother liquor was diluted with a large quantity of water to precipitate the monoglycinoquinone. The latter was filtered and washed with water and ether. After air-drying, weight 1.7 g.

Diglycinoquinone forms a black, friable, microcrystalline powder, outwardly resembling monoglycinoquinone. Unlike the latter, it is substantially insoluble in ethanol. It dissolves with difficulty in glacial acetic acid. When heated in a capillary it decomposes without melting. It dissolves completely in dilute solutions of sodium carbonate and NaOH, forming, like monoglycinoquinone, a solution of the sodium salt from which it can again be precipitated by acidification. Addition of $AgNO_3$ solution to the sodium salt solution gives the insoluble silver salt of diglycinoquinone. The latter was analyzed in the following manner: 0.98 g diglycinoquinone, thoroughly washed with ethanol, was dissolved in 18.7 ml (2 equivs.) of exactly 0.1 N NaOH, and to the obtained solution was added a solution of 1.31 g (2 equivs.) $AgNO_3$ in 50 ml water. The next day the precipitated silver salt was filtered, washed with water, alcohol and ether and dried at 120°. It was then in the form of a black powder with a metallic luster. Diglycinoquinone is not modified by treatment with boiling dilute HCl; it is quite stable in boiling dilute alkalies.

0.1036, 0.1196 g sub.: 8.96, 9.87 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 11.33, 11.56. $C_{10}H_{10}O_6N_2$. Calculated %: N 11.02.

Analysis of silver salt for silver:

0.2396, 0.2129 g sub.: 0.1535, 0.1324 g AgCl. Found %: Ag 46.56, 46.87. $C_{10}H_8O_6N_2Ag_2$. Calculated %: Ag 46.15.

Preparation of Diglycinoquinone by Saponification of its Diethyl Ester

2 g diethyl ester of diglycinoquinone (m.p. 210°), prepared by condensation of benzoquinone with ethyl glycinate [3], was introduced into 48 ml 0.5 N Na_2CO_3. The mixture was heated on a water bath to complete solution of the ester. The brown-red solution was filtered and then acidified with 10% HCl to an acidic reaction. The precipatated diglycinoquinone was filtered, washed with hot water and ethanol, and dried at 120°. Yield 0.5 g (30.5%).

The diglycinoquinone was identical in all properties with the compound synthesized by condensation of benzoquinone with glycine.

0.0906, 0.0748 g sub.: 7.12, 5.92 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 11.02, 11.07. $C_{10}H_{10}O_6N_2$. Calculated %: N 11.02.

II. Condensation of p-Benzoquinone with α-Alanine

Monoalaninoquinone

5.4 g (2 moles) benzoquinone was dissolved at 50° in 200 ml water. To the solution was added dropwise, with vigorous stirring, a solution of 2.2 g (1 mole) alanine in 50 ml water and the mixture was stirred at the same temperature for 6 hours. The next day the precipitated monoalaninoquinone was filtered from the brown mother liquor, repeatedly washed with hot water, then with ether, and dried. Yield 1.2 g (25 %). For analysis the substance was reprecipitated from ethanolic (or alkaline) solution.

Monoalaninoquinone forms a black powder, similar in properties to monoglycinoquinone.

0.1190, 0.1480 g sub.: 6.33, 7.71 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 7.30, 7.22. $C_9H_9O_4N$. Calculated %: N 7.18.

Dialaninoquinone

To a solution of 8.1 g (3 moles) benzoquinone in 300 ml ethanol, heated to 60°, was added dropwise with vigorous stirring a solution of 4.4 g (2 moles) alanine in 50 ml water. Stirring and heating were continued for 9 hours, after which the mixture was left overnight at room temperature. The next day the precipitate of dialaninoquinone, appreciably contaminated with unreacted alanine, was filtered from the dark-brown mother liquor, washed with hot ethanol, then with water, once again with ethanol and finally with ether. The precipitate was detached from the filter and ground in a mortar; it was covered with ethanol and left for several hours. Then the dialaninoquinone was filtered again and washed with ethanol until a perfectly colorless filtrate ran through the funnel. Yield 1 g (15%). For analysis the dialaninoquinone was reprecipitated from alkaline solution, washed with water and dried at 120°. Dialaninoquinone is a black powder. Unlike monoalaninoquinone it is insoluble in ethanol. Its properties are similar to those of diglycinoquinone.

0.1244, 0.1152 g sub.: 8.43, 8.11 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 9.34, 9.48. $C_{12}H_{14}O_6N_2$. Calculated %: N 9.90.

SUMMARY

Reaction between p-benzoquinone and α-amino acids results, apart from the oxidative cleavage of the amino acids described in the literature, in formation of products of condensation of the acids with p-benzoquinone of the type usual for quinones.

From p-benzoquinone and glycine were obtained mono- and diglycinoquinones; correspondingly, p-benzoquinone with α-alanine yielded mono- and dialaninoquinones.

Products of condensation of 1 molecule of p-benzoquinone with 1 molecule of amino acid are obtained by carrying out the reaction in aqueous solution; since they are insoluble in water they are precipitated. Products of condensation of 1 molecule of quinone with two molecules of amino acid were obtained by carrying out the reaction in ethanolic solution.

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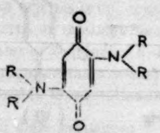
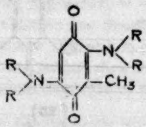
QUINONES

VII. REACTION OF CHLORO DERIVATIVES OF p-BENZOQUINONE WITH ETHYL GLYCINATE

I.S. Ioffe and Z.Ya. Khavin

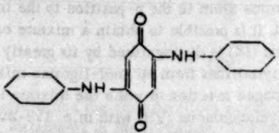
In the preceding communication [1] we considered the reaction of p-benzoquinone with amino compounds leading to addition of amino radicals to carbon atoms of the quinoid nucleus. This reaction usually culminates in the formation of diamino derivatives of the quinone containing both amino groups, as a rule, in the p-position to one another. The compounds are of the general type (I):

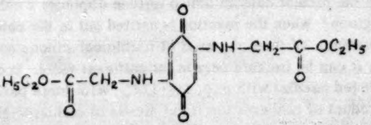

(I)


(II)

Like benzoquinone, toluquinone also adds on two amino groups with formation of compounds of type (II). The methyl group has no appreciable influence upon the course of the reaction. On reaction of amines with chloroquinones [2,3,4], however, amino radicals not only add on to the unsubstituted carbon atoms but they also displace the chlorine atoms. Literature data on this subject, however, are contradictory. According to one report [2] treatment of chloroquinone with amines gives chlorine-free diaminoquinones, whereas elsewhere [3] the formation of chlorodiaminoquinones is reported. Again, trichloroquinone is reported [3] to lose one chlorine atom to form dichlorodiaminoquinones, while other workers [4] claim to displace two atoms of chlorine to obtain monochlorodiaminoquinones.

This problem has been studied most closely by Niemeyer [2] who condensed various quinones with aniline and toluidine. All the products that he obtained by this condensation, however, resemble dianilinoquinone (III) in being poorly soluble in organic solvents, in not being readily amenable to purification by crystallization, and in melting unsharply at above 300°. Niemeyer was, therefore, unable to accurately establish the course of the reaction of chloroquinones with amines.


(III)

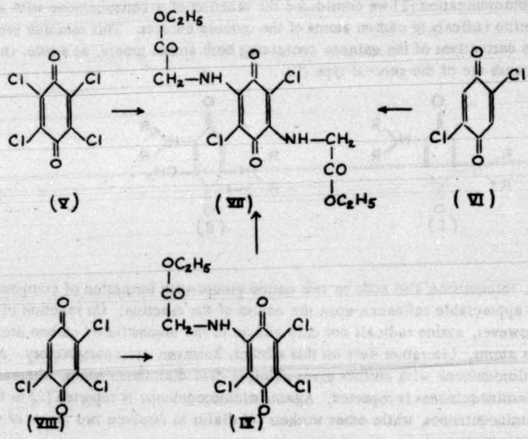

(IV)

Of the diamino derivatives of quinone, the product of condensation with ethyl glycinate (IV) [5], described in the preceding communication [1], is distinguished by the ability to crystallize well from organic solvents, by high stability, and by the relatively low and sharp m.p. of 210°; we, therefore, carried out the condensation of ethyl glycinate with various chloroquinones. By carrying out this reaction in a variety of conditions, we were able, moreover, to segregate the introduction of amino radicals at unsubstituted carbon atoms of the quinoid nucleus from the displacement of chlorine atoms by amino groups, and, thereby, were able to compare both of these directions of the reaction.

The reaction proceeds the most smoothly with tetrachloroquinone (V). On mixing solutions, heated to 60°, of ethyl glycinate and tetrachloroquinone in ethyl acetate, a violet-red color is developed whose intensity increases with further heating. On cooling, a precipitate comes down and consists of a mixture of glycine hydrochloride and the product of condensation of the starting components. The product was purified by crystallization from ethyl acetate and separated in the form of brick-red clusters with constant m.p. of 199-120°.

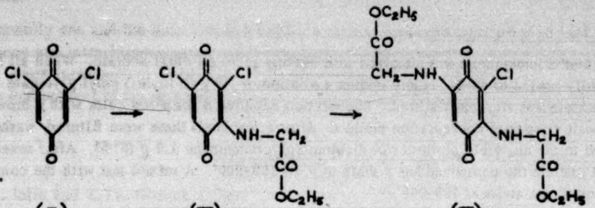
Analysis showed that this substance contains two chlorine atoms and two ethyl glycinate residues. The relative positions of the substituents was established by the observation that the identical substance is obtained on condensing ethyl glycinate with 2,5-dichloroquinone (VI). Hence, the reaction of tetrachloroquinone with the amine results in displacement of the two atoms of chlorine in the p-position to one another, and the product is the diethyl ester of 2,5-dichloro-3,6-diglycinoquinone with the structure (VII).

The mode of formation of this dichlorodiaminoquinone (VII) from tetrachloroquinone differs fundamentally, however, from the mode of formation from 2,5-dichloroquinone. With 2,5-dichloroquinone the reaction follows the course usual for quinones, the amino residues adding onto the unsubstituted carbon atoms of the quinoid nucleus; this reaction takes place quickly at a moderate temperature. In the reaction with tetrachloroquinone, however, 2 amino residues displace 2 chlorine atoms in the p-position to one another. Heating is needed to speed up this reaction.



When ethyl glycinate reacts with trichloroquinone (VIII) the reaction proceeds in both of the above-described directions. At first an amino residue adds on to the sole unsubstituted carbon atom of the trichloroquinone molecule with formation of the ester of trichloroglycinoquinone (IX). At the same time, however, displacement of one of the chlorine atoms by still another amino residue takes place. The resultant product melts at 199-200° and is identical with the above-described diester of dichlorodiglycinoquinone (VII). From this it follows that also in the present case an amino residue displaces a chlorine atom in the p-position to the initially introduced amino group. When the reaction is carried out in the cold, it is possible to obtain a mixture of both products of condensation. Of these the ester of trichloroglycinoquinone (IX) is distinguished by its greatly superior solubility; it can be isolated only in insignificant yield. It crystallizes from ethanol-ligroine mixture in the form of dark-red needles with m.p. 111-112°. With more prolonged reaction or when the mixture is heated, the sole product of condensation is the diester of dichlorodiglycinoquinone (VII) with m.p. 199-200°.

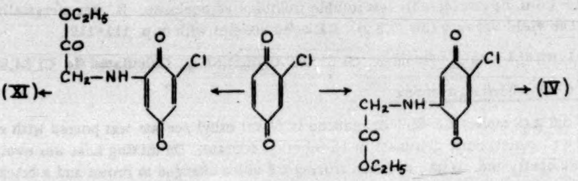
Mixing of the ethyl acetate solutions of 2,6-dichloroquinone (X) and ethyl glycinate gave a condensation product whose analysis revealed the presence of 1 chlorine atom and 2 amino residues; it was evidently the diester of 2-chloro-3,6-diglycinoquinone (XI). This substance is poorly soluble in ethyl acetate and crystallizes as bright-red clusters with constant m.p. of 189-190°. As in the case of reaction with trichloroquinone, the formation of this substance involves addition of an amino residue to one of the equivalent unsubstituted carbon atoms of the 2,6-dichloroquinone molecule and displacement of an atom of chlorine in the p-position to this amino group by another amino residue. Our observations reveal that also in this case the addition of the amino residue to the unsubstituted carbon atom with formation of the ester of 2,6-dichloro-3-glycinoquinone (XII) proceeds with a higher velocity, but we were unable to obtain this intermediate product in the pure form. During the reaction it changes into the diamino derivative (XI). When the reaction is carried out for a short period in the cold, however, the amount of monoamino derivative (XII) formed is small; it is very soluble in organic solvents and even in water; hence attempts to isolate this substance and to crystallize it were unsuccessful.



(X) (XII) (XI)

The course of the reaction of ethyl glycinate with monochloroquinone (XIII) was more complex. Mixing and moderate heating of ethyl acetate solutions of these substances results in precipitation of a dark-red chlorine-containing product. In different experiments its m.p. varied between 180 and 190°. It crystallizes from ethyl acetate but the m.p. of the crystals is not constant; in some experiments it reaches 200°. No marked depression of melting point was observed on mixing either with the chlorine-free diester of the diglycinoquinone (IV) with m.p. 210° or with the diester of 2-chloro-3,6-diglycinoquinone (XI) with m.p. 189-190°. Analytical determinations of chlorine and amino nitrogen in the repeatedly crystallized product show that is a mixture of compounds (IV) and (XI) which is not amenable to resolution in the conditions employed by us.

Formation of both of these substances on reaction of chloroquinone with ethyl glycinate can be explained in the following manner. At first an amino residue must add on to one of the unsubstituted carbon atoms of (XIII). Under the dual electronic influence of the halogen, the amino group can enter both in the p-position to the chlorine with formation of 2-chloro-5-aminoquinone (XIV) and in the m-position with formation of 2-chloro-6-aminoquinone (XV). Each of these intermediately formed substances, however, can easily take up another amino residue but now, as a rule, in the p-position to the original amino group. For 2-chloro-5-aminoquinone (XIV) this reaction proceeds with displacement of the halogen and with formation of the halogen-free diester of diglycinoquinone (IV). In the 2-chloro-6-amino compound (XV) the amino group adds on to the unsubstituted carbon atom in the 3-position with formation of the diester of 2-chloro-3,6-diglycinoquinone (XI). The mixture of these substances is also the end product of the reaction of chloroquinone with ethyl glycinate:



(XV) (XIII) (XIV)

Our results and the considerations advanced in the course of their evaluation allow us to clear up the conflicting statements in the literature. Our observations on the reaction of chloroquinones with ethyl glycinate are also in accord with some special cases of condensation of chloroquinones with amines described in the literature [6-10].

EXPERIMENTAL

Reaction of Tetrachloroquinone

3 g (1 mole) tetrachloroquinone was dissolved at 60° in 225 ml ethyl acetate. To the solution at the same temperature was added a solution of 2.5 g (2 moles) ethyl glycinate in 10 ml ethyl acetate. The mixture of solutions acquired a violet-red color. After standing and cooling, the diester of dichlorodiglycinoquinone came down in admixture with samll white needles of ethyl glycinate hydrochloride. The condensation product was extracted with boiling ethyl acetate in which ethyl glycinate hydrochloride is substantially insoluble.

Cooling of the filtered, hot solution brought down the diester of dichlorodiglycinoquinone in quantity of 2.3 g or 50% of the theoretical yield. It forms clusters with a characteristic, somewhat whitish, brick-red color. After repeated crystallization its m.p. is constant at 199-200°.

0,1710, 0,1606 g sub.: 0,1298, 0,1204 g AgCl. Found %: Cl 18,79, 18,56. $C_{14}H_{16}O_6N_2Cl_2$. Calculated %: Cl 18,73.

Reaction of 2,5-Dichloroquinone

4 g (3 moles) 2,5-dichloroquinone was dissolved with heating in 70 ml ethyl acetate. When all had dissolved, the solution was carefully cooled to 40-50° before adding a solution of 1.8 g (2 moles) ethyl glycinate in 10 ml ethyl acetate. The mixture was vigorously stirred. The solution acquired a deep-red color with a brownish tinge and soon began to deposit crystals of condensation product. After a few hours these were filtered, washed with ethyl acetate and dried in the air; yield of diester of dichlorodiglycinoquinone 1.9 g (67%). After several crystallizations from ethyl acetate the compound has a sharp m.p. of 199-200°. A mixed test with the compound obtained from tetrachloroquinone melts at 199-200°.

0,1715, 0,1695 g sub.: 0,1274, 0,1272 g AgCl. Found %: Cl 18,40, 18,58. $C_{14}H_{16}O_6N_2Cl_2$. Calculated %: Cl 18,73.

Reaction of Trichloroquinone

a) To a solution of 3 g (2 moles) trichloroquinone in 40 ml ethyl acetate, heated to boiling, was added 2 g (3 moles) ethyl glycinate in 15 ml ethyl acetate; the mixture acquired a dark-red color. Cooling brought down a mixture of condensation product and ethyl glycinate hydrochloride. Extraction with ethyl acetate yielded 1.36 g of the diester of dichlorodiglycinoquinone (50.4%). After the first crystallization the substance melted at 185-188°; after the second at 199-200°. A mixed test with the substance obtained from tetrachloroquinone and from 2,5-dichloroquinone melted at 199-200°.

0,1685, 0,1532 g sub.: 0,1260, 0,1154 g AgCl. Found %: Cl 18,51, 18,65. $C_{14}H_{16}O_6N_2Cl_2$. Calculated %: Cl 18,73.

b) 5 g (2 moles) trichloroquinone was dissolved in 100 ml ethyl acetate and the solution was cooled with ice and salt; with vigorous stirring dropwise addition was made of a solution of 1.2 g (1 mole) ethyl glycinate in 30 ml ethyl acetate. The dark-cherry solution was kept for another 3-4 hours(cooled with iced water) and then left overnight at room temperature. In the solution was found only an insignificant deposit which was filtered off. The ethyl acetate was driven off from the cherry-red filtrate in vacuum, and the residue was dried in a vacuum-desiccator.

Fractional crystallization from alcohol enabled separation of the condensation product – the ester of trichloroglycinoquinone – from the considerably less soluble trichlorohydroquinone. It was recrystallized from alcohol-ligroine mixture. The yield was very low (0.9 g). Dark-red needles with m.p. 111-112°.

0,1126 g sub.: 0,1414 g AgCl. Found %: Cl 31,09. $C_{10}H_8O_4NCl_3$. Calculated %: Cl 34,08.

Reaction of 2,6-Dichloroquinone

A solution of 3,3 g (2 moles) 2,6-dichloroquinone in 50 ml ethyl acetate was poured with energetic stirring into a solution of 3 g (3 moles) ethyl glycinate in 15 ml ethyl acetate. On mixing heat was evolved and the solution became dark cherry-red. With continued stirring the color changed to brown and a brick-red precipitate of the condensation product – the diester of chlorodiglycinoquinone – separated from the solution. After keeping overnight, it was filtered off, washed with cold ethyl acetate and dried. Yield 3 g (94%). Very sparingly soluble in ethyl acetate, almost insoluble in ethanol and ether. After recrystallization from excess of boiling ethyl acetate it formed very beautiful, bright-red, lustrous clusters with sharp m.p. of 189-190°.

0,1518, 0,1629 g sub.: 0.0631, 0.0679 g AgCl. Found %: Cl 10.28, 10.32. $C_{14}H_{17}O_6N_2Cl$. Calculated %: Cl 10,30.

SUMMARY

The reaction of chloroquinones with amines culminates, like the reaction with the unsubstituted quinone, in formation of the diamino derivative of the quinone containing, as a rule, both amino groups in the p-position to one another. Depending upon the number of halogen atoms and their relative positions, this reaction proceeds according to two different mechanisms in two directions involving respectively addition of amino residues to the unsubstituted carbon atoms of the quinoid nucleus and displacement of halogen atoms by amino residues.

The amino residues add on to the unsubstituted carbon atoms of the quinoid nucleus with greater velocity and in milder conditions. If the carbon atoms in the p-position to one another are free, then amino residues add on to both. If a chlorine atom is attached to the carbon atom in the p-position to the added-on amino residue, then the chlorine atom is displaced by another amino residue. Chlorine atoms in the o- and m-positions to the amino group are stable. In tetrachloroquinone 2 chlorine atoms in the p-position to one another are displaced by amino residues.

Consequently one and the same 2,5-dichloro-3,6-diamino derivative is formed from 2,5-dichloroquinone, trichloroquinone and tetrachloroquinone; 2,6-dichloroquinone gives the 2-chloro-3,6- derivative; from monochloroquinone, where intermediate addition of an amino residue is possible in both the p- and m-position to the chlorine, the end product of the reaction is a mixture of 3,6-diaminoquinone and the 2-chloro-3,6-diamino derivative.

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* See Consultants Bureau Translation, p. 533.

[illegible] to one another are inclined to [illegible] amino reaction.

Consequently one and the same [illegible] [illegible] [illegible] which [illegible] chlorine, the end-product of the reaction is a mixture of [illegible]

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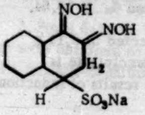
* See Consultants Bureau Translation, [illegible]

INVESTIGATIONS IN THE 1,2-NAPHTHO-(3',4')-FURAZAN SERIES

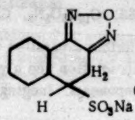
III. THE BISULFITE COMPOUND OF 1,2-NAPHTHO-(3',4')-FURAZAN AND 6-NITRO-1,2-NAPHTHO-(3',4')-FURAZAN

S.V. Bogdanov and S.F. Petrov

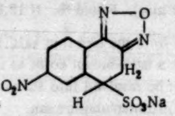
It has been observed [1] that boiling of the bisulfite compound 1,2-naphthoquinonedioxime (I) with sodium carbonate solution converts it into 1,2-naphtho-(3',4')-furazan (1,2-naphthoquinonedioxime anhydride). It appeared probable that the first step in the reaction is scission of the bisulfite compound into sulfite and 1,2-naphthoquinonedioxime, and the second step the dehydration of naphthoquinonedioxime to naphthofurazan. The bisulfite compound actually undergoes scission in this manner with sodium hydroxide. On the other hand we cannot exclude the possibility of preliminary dehydration of the bisulfite compound of naphthoquinonedioxime to the bisulfite compound of naphthofurazan followed by cleavage of bisulfite. Experiments showed that heating of a solution of the bisulfite compound of naphthoquinonedioxime with a very slight excess of sodium carbonate at 60-100° actually led to the bisulfite compound of 1,2-naphtho-(3',4')-furazan (II). Further treatment of this bisulfite compound with sodium carbonate or sodium hydroxide splits it into sulfite and naphthofurazan. In an acid medium the bond between sulfurous acid and the naphthofurazan molecule is so strong that when the bisulfite compound of naphthofurazan in sulfuric acid solution is treated with nitric acid, it is converted into the nitro compound without cleavage of sulfurous acid. Whereas the main products of nitration of free 1,2-naphtho-(3',4')-furzan are 5- and 7-nitronaphthofurazans [2], substitution here occurs mainly in the 6-position. The resultant bisulfite compound of 6-nitro-1,2-naphtho-(3',4')-furazan (III) is converted by the action of caustic alkali into 6-nitronaphthofurazan (IV), while its reduction gives the bisulfite compound of aminonaphthofurazan.



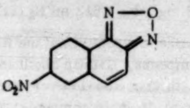
(I)



(II)



(III)



(IV)

The structure of 6-nitronaphthofurazan was established by its conversion into 6-aminonaphthofurazan and then (via the diazo compound) into naphthofurazan-6-sulfonic acid; also by comparison with the naphthofurazan-6-sulfonic acid obtained from 1-nitroso-2-naphthol-6-sulfonic acid via 1,2-naphthoquinonedioxime-6-sulfonic acid [3].

The diazo compound from 6-aminonaphthofurazan was also transformed into 6-chloro- and 6-hydroxynaphthofurazan.

Attempts to prepare the bisulfite compound of naphthofurazan by treatment of naphthofurazan with 5 times the quantity of bisulfite in an aqueous ethanolic medium by boiling or by heating in a tube at 170° were unsuccessful.

EXPERIMENTAL

Bisulfite Compound of 1,2-naphtho-(3',4')-furazan. Into 73 ml sodium carbonate solution containing 5.4 g sodium carbonate was introduced at 20° 27 g of the sulfite of 1,2-naphthoquinonedioxime. The solution was boiled for an hour and then cooled. The grey bisulfite compound was filtered and washed with water, ethanol and ether; yield 24.2 g (73.8%).

On adding the sulfite compound to a solution of sodium carbonate heated to 60 or 70° and holding the solution for 2 hours at the same temperature, the yield of bisulfite compound of naphthofurazan was 7.8 and 16.78 g. Small amounts of naphthofurzan were formed in all the experiments. The colorless rectangular plates (from aqueous ethanol) are readily soluble in water, insoluble in organic solvents.

0.9967 g sub.: loss on drying (170°) 0.1635 g. 0.2560 g dry. sub.: 0.0662 g Na_2SO_4. 6.814 mg sub.: 9.150 mg CO_2; 2.404 mg H_2O. 2.917 mg sub.: 0.236 ml N_2 (30°, 725 mm). Found %: H_2O 16.40; Na 8.37; C 36.64; H 3.95; N 8.70. $C_{10}H_7O_4N_2SNa \cdot 3H_2O$. Calculated %: H_2O 16.46; C 36.58; H 3.99; N 8.53. $C_{10}H_7O_4N_2SNa$. Calculated %: Na 8.39.

Nitration of the bisulfite compound. To a solution of 18.25 g (0.0666 mole) bisulfite compound (dried at 170°) in 125 ml conc. sulfuric acid was added, at -2°, a mixture of 4.37 g (0.0687 mole) 99.1% nitric acid and 26 ml sulfuric acid in the course of an hour. The reaction mass was stirred 2 hours and poured into 1500 g ice. The solution was neutralized with calcium carbonate, the calcium sulfate was filtered off, and the filtrate evaporated to dryness. For removal of traces of gypsum the residue was treated with a small amount of hot water, and the solution was filtered and again evaporated to dryness. Weight of residue (dried at 150°) 21.6 g; it was a mixture of the sodium salt and a small amount of calcium salt. This mixture was treated with 220 ml boiling ethanol and the calcium salt filtered off; weight of latter (dried at 150°) 1.3 g. Colorless, short prisms (from water), poorly soluble in cold water and readily in hot water, very sparingly soluble in ethanol.

0.3372 g sub.: loss on drying (170°) 0.0414 g. 7.934 mg sub.: 9.642 mg CO_2; 2.330 mg H_2O. 2.752 mg sub.: 0.292 ml N_2 (29°, 726 mm). Found %: H_2O 12.27; C 33.16; H 3.29; N 11.47. $C_{20}H_{12}O_{12}N_6S_2Ca \cdot 5H_2O$ Calculated %: H_2O 12.47; C 33.24; H 3.07; N 11.63.

Partial evaporation of the filtrate from the calcium salt led to separation of 13.5 g (after drying at 150°) sodium salt of the bisulfite compound.

Long colorless prisms (from ethanol), readily soluble in water, less soluble in ethanol.

0.4138 g sub.: loss on drying (170°) 0.0425 g. 6.684 mg sub.: 8.252 mg CO_2; 1.690 mg H_2O. 3.410 mg sub.: 0.370 ml N_2 (22°, 729 mm). Found %: H_2O 10.27; C 33.67; H 2.83; N 12.04. $C_{10}H_6O_8N_3SNa \cdot 2H_2O$. Calculated %: H_2O 10.14; C 33.80; H 2.84; N 11.82.

When the calcium and sodium salts of the bisulfite compound are heated with 0.5 N NaOH, they break down with formation of 6-nitronaphthofurazan and sulfite. 6-Nitronaphthofurazan crystallizes from acetic acid in the form of needles, m.p. 202.7-203.7°, readily soluble in acetic acid and very much less soluble in ethanol.

3.483 mg sub.: 0.613 ml N_2 (21°, 730 mm). Found %: N 19.63. $C_{10}H_5O_3N_3$. Calculated %: N 19.54.

On further evaporation of the filtrate from the calcium salt, further separation was effected of 6.11 g bisulfite compound. Caustic alkali imparts a dark-brown color to its solution and a yellow precipitate is separated with m.p. 165-177°. It could not be resolved into its components. Judging by the results of reduction of this mixture, its main component was 6-nitronaphthofurazan.

6-Aminonaphthofurazan a) Into a solution of 5.33 g sodium salt of the bisulfite compound of nitronaphthofurazan in 50 ml water, acidified with 0.25 ml 60% acetic acid, was introduced 2.2 g iron filings at 75° in the course of 30 minutes; the mixture was then held at 75° for 1 and a half hours. After addition of magnesia, the sludge was filtered off, the filtrate was evaporated to dryness, and the residue was crystallized from water; yield 0.77 g. The bisulfite compound of aminonaphthofurazan forms greenish needles, readily soluble in water and less readily in ethanol. Heating with 5% NaOH liberates the free amino compound with m.p. 172.8-173.1°.

b) 6-Nitronaphthofurazan was reduced on the same lines as the product of nitration of naphthofurazan [2].

Using Fe turnings 8.6 g (0.04 mole) nitro compound gave 6.7 g aminonaphthofurazan with m.p. 172.1-172.8°. Using sodium sulfite as reducing agent, 1.85 g nitro compound gave 0.96 g amino compound with m.p. 170.9-171.8° and 0.45 g by-product insoluble in hydrochloric acid. Yellow needles (from ethanol) with m.p. 173.1-173.7°, readily soluble in ethanol and benzene.

3.275 mg sub.: 0.665 ml N_2 (24°, 735 mm). Found %: N 22.57. $C_{10}H_7ON_3$. Calculated %: N 22.70.

The hydrochloride (from 4% hydrochloric acid) forms colorless needles, considerably more stable than the salts of 5- and 7-aminonaphthofurazans.

6-Chloronaphthofurazan. To a suspension of 1.85 g (0.01 mole) 6-aminonaphthofurazan in 120 ml 4% HCl at 0-5° was added a solution of 0.76 g sodium nitrite in 20 ml water. The solution of the diazo compound was run into a solution (heated to 70-80°) of 3.2 g cuprous chloride in 48 ml 36% HCl and 16 ml water. After stirring for 30 minutes at 70-80°, the mixture was cooled, and the chloronaphthofurazan was filtered off; yield 1.83 g. Colorless needles (from isobutyl alcohol), m.p. 148-148.3°. Dissolves readily in ethanol, isobutyl alcohol, chlorobenzene and acetic acid.

3.061 mg sub.: 0.383 ml N_2 (31°, 734 mm). Found %: N 13.57. $C_{10}H_5ON_2Cl$. Calculated %: N 13.70.

6-Hydroxynaphthofurazan Preparation was by the same procedure as for 7-hydroxynaphthofurazan [2] from 2.77 g 6-aminonaphthofurazan; yield 2.19 g.

Light-yellow needles (from methanol), m.p. 190.2-190.9°. Readily soluble in organic solvents.

3.777 mg sub.: 0.510 ml N_2 (21°, 730 mm). Found %: N 15.06. $C_{10}H_6O_2N_2$. Calculated %: N 15.05.

Naphthofurazan-6-sulfonic acid a) A sulfuric acid solution of the diazo compound prepared from 3.33 g 6-aminonaphthofurazan was treated as already described for 5-diazonaphthofurazan [2]. Yield of sodium salt of the sulfonic acid 4.15 g. Colorless rhombic plates (from water), readily soluble in water.

0.2700 g substance: loss on drying (120°) 0.0316 g. 0.2693 g dry sub.: 0.0703 g Na_2SO_4. Found %: H_2O 11.70; Na 8.45. $C_{10}H_5O_4N_2SNa \cdot 2H_2O$. Calculated %: H_2O 11.69. $C_{10}H_5O_4N_2SNa$. Calculated %: Na 8.45.

Sulfochloride. Elongated rhombic plates (from chlorobenzene), m.p. 202.2-202.3°.

Amide. Needles (from chlorobenzene), m.p. 245.8-246.5°.

2.851 mg sub.: 0.438 ml N_2 (27°, 728 mm). Found %: N 16.75. $C_{10}H_7O_3N_3S$. Calculated %: N 16.86.

b) A solution of 36.2 g (0.1 mole) sodium salt of 1,2-naphthoquinonedioxime-6-sulfonic acid in 320 ml 10% NaOH solution was boiled for an hour and cooled. The separated sodium salt of naphthofurazan-6-sulfonic acid was filtered; yield 29.48 g.

Sulfochloride. Elongated rhombic plates (from chlorobenzene), m.p. 202.8-203.7°. Melting point of mixture of sulfochlorides 202.5-203.4°.

Amide. Needles (from chlorobenzene), m.p. 246-247°. Melting point of mixture of amides 246-246.7°.

SUMMARY

1. Heating of a solution of the bisulfite compound of 1,2-naphthoquinonedioxime with a small quantity of sodium carbonate gives the bisulfite compound of 1,2-naphtho-(3',4')-furzan.

2. The bisulfite compound of 1,2-naphtho-(3',4')-furazan is converted on nitration into the bisulfite compound of 6-nitro-1,2-naphtho-(3',4')-furazan.

3. From 6-nitro-1,2-naphtho-(3',4')-furazan was obtained 6-amino-1,2-naphtho-(3',4')-furazan; from the latter were obtained 6-chloro-1,2-naphtho-(3',4')-furazan, 6-hydroxy-1,2-naphtho-(3',4')-furazan, and 1,2-naphtho-(3',4')-furazan-6-sulfonic acid.

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* See Consultants Bureau Translation, p. 395.

4.178 mg subst.: [illegible] ml N_2 ([illegible]). Found %: N [illegible]. [illegible] Calculated %: N 9.16.

Naphthalene-2-sulfonic acid. a) A [illegible] acid solution of [illegible] the [illegible] acid [illegible] 3.15 g. Colorless rhombic plates (from water), readily soluble in water.

0.2755 g substance: loss on drying [illegible]. Found %: [illegible] 11.10. [illegible] Calculated %: [illegible]

[illegible] Elongated rhombic plates (from [illegible]), m.p. [illegible]

Anilide. Needles (from chloroform), m.p. [illegible]

2.5[illegible] mg subst.: [illegible] ml N_2 ([illegible]). Found %: N [illegible]. Calculated %: N [illegible]

b) A solution of 36.9 g (0.1 mole) [illegible] was boiled for an hour [illegible] yield 22.52 g.

Sulfochloride. [illegible] prisms (from [illegible]), m.p. [illegible]; literature data [illegible] sulfochloride m.p. [illegible]

Amide. [illegible] m.p. [illegible]

SUMMARY

1. Heating of a solution of the bicyclic compound [illegible]

2. The bicyclic compound [illegible]

3. From [illegible]

LITERATURE CITED

[1] S. Hoffmann, J. Gen. Chem. [illegible]

[2] [illegible]

[3] [illegible]

4. [illegible]

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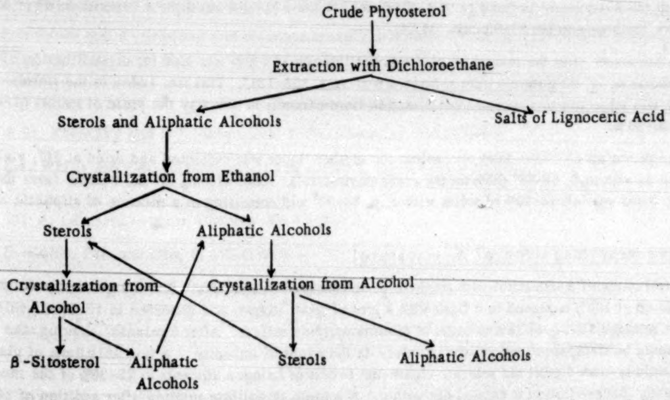
* See Consultants Bureau Translation, p. 96.

ISOLATION OF β-SITOSTEROL FROM CRUDE PHYTOSTEROL AND ITS ANALYSIS

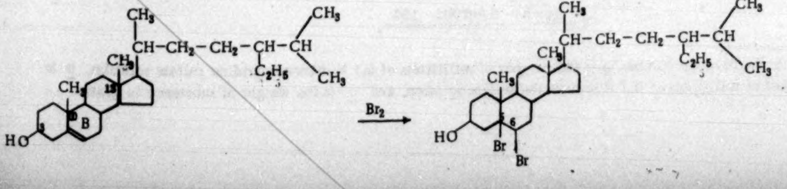
A.M. Khaletsky and I.M. Yurist

In the preceding investigation [1] it was shown that crude phytosterol, obtained by alkaline hydrolysis of pinewood, is a mixture of sterols, higher aliphatic alcohols and salts of higher molecular acids, the predominant components being β-sitosterol, lignoceryl alcohol, and salts of lignoceric acid. It was of interest to establish convenient methods of isolation of β-sitosterol with avoidance under industrial conditions of extraction of crude phytosterol with ether and of benzoylation of the isolated sterols. Numerous experiments led to the conclusion that extraction of sterols and aliphatic alcohols with ether may be replaced by extraction with dichloroethane, while β-sitosterol could be separated from sterols by recrystallization from alcohol according to the scheme given below.

In working up large amounts of crude phytosterol, it is expedient to crystallize the fraction containing the sterols and aliphatic alcohols from the mother liquor remaining after a second crystallization of the sterols, and to add the separated sterols to those previously isolated and to crystallize them from ethanol. In this manner isolation was effected from crude phytosterol of about 30% β-sitosterol with m.p. 134-136°, over 40% of the aliphatic alcohols in admixture with other sterols, and over 20% of the salts of lignoceric acid; about 10% consisted of inorganic substances and moisture. The β-sitosterol isolated from crude phytosterol merits interest in that in its molecule the spatial arrangement of the rings and of the individual groups (angular methyl groups at C_{10} and C_{13} and secondary alcoholic grouping at C_3, as well as the double bond at $C_5—C_6$) is the same as in chloesterol, only differing in that at C_{24} there is an additional alkyl group - C_2H_5 [2]. Not less interest is presented by the aliphatic alcohols and acids containing hydrocarbon radicals with 23 C atoms; as far as we know, such compounds are important for the synthesis of antitubercular and antileprous agents [3] and were formerly difficultly accessible.


Crude Phytosterol
Extraction with Dichloroethane
Sterols and Aliphatic Alcohols
Salts of Lignoceric Acid
Crystallization from Ethanol
Sterols
Aliphatic Alcohols
Crystallization from Alcohol
Crystallization from Alcohol
β-Sitosterol
Aliphatic Alcohols
Sterols
Aliphatic Alcohols

For the purpose of quantitative determination of β-sitosterol we utilized its behavior with bromine. Bromine adds on quantitatively at the double bond of ring B with formation of the 5,6-dibromo derivative:


CH₃
CH-CH₂-CH₂-CH-CH
CH₃
C₂H₅
CH₃
CH₃
CH₃
13
10
3
B
HO
Br₂
CH₃
CH-CH₂-CH₂-CH-CH
CH₃
C₂H₅
CH₃
CH₃
CH₃
5
6
HO
Br
Br

Of the various methods of halogenation the best results were obtained by bromination of β-sitosterol with dibromopyridine sulfate in solution in glacial acetic acid (analogous to the determination of cholesterol [4]) or by the bromide-bromate method [5].

EXPERIMENTAL

Crude Phytosterol

Crude phytosterol is a coarsely crystalline powder with a yellowish-grey color and a greasy luster. Addition of acetic anhydride and conc. sulfuric acid to is saturated chloroform solution brings about an intensification of color with passage through various tints from pink to blue-green. The bromine number is 21, the m.p. 80-130°; moisture content 5%; the proportion soluble in dichloroethane is 74%; the residue insoluble in dichloroethane amounts to 21%. The substance extracted with dichloroethane melts at 82-120°. Recrystallization from ethanol gives two fractions-sterols and aliphatic alcohols. Recrystallization from 18 times the amount of ethanol ensures the optimum conditions for resolution of the fractions, good filterability, and a relatively high degree of purity of the sterols. Repeated crystallization from 18 times the amount of ethanol makes possible the isolation of pure β-sitosterol with m.p. 134-136°.

Separation of β-Sitosterol from Crude Phytosterol

350 g crude phytosterol (corresponding to 370 g starting material), dried at 80°, was subjected to extraction in a Soxhlet apparatus with 1500 ml dichloroethane for 25-30 hours until a sample from the extractor just gave a very small precipitate (not more than 0.02 g from 1 ml dichloroethane extract withdrawn from the extractor with a pipet). At the end of the extraction the insoluble residue (salts of lignoceric acid) were separated, and the filtrate was conbined with the dichloroethane extract; the yield of dry residue insoluble in dichloroethane amounted to 77-78 g (21% on the crude phytosterol). Distillation of the dichloroethane, at first at the ordinary pressure and towards the end at 100 mm, gave 272 g substance (77.7%) which was dissolved in 5 liters ethanol with refluxing and stirring. At 38-40° the solution was filtered through a heated porcelain funnel. The sterols collected on the filter were dried at 60-65°; yield 96 g (35% on the dry dichloroethane extract), m.p. 133-136°.

On cooling, the filtrate deposited the aliphatic alcohols contaminated with sterols; separation yielded 125 g dry substances melting at 67-100°.

96 g sterols were crystallized from 1700 ml ethanol to give 85 g of a substance with m.p. 134-136°. A mixed test with the β-sitosterol isolated from β-sitosterol benzoate [1] did not show a depression; $[\alpha]_D - 35°$ (in chloroform); bromine number 37-39; calc. 38.57.

The mother liquor after the second ethanolic crystallization (d 0.82) was used for crystallization of the aliphatic alcohols; at 40° 23 g sterols were separated with m.p. 126-131°. This was added to the sterols fraction which was subjected to a second crystallization from ethanol; in this way the yield of sterols (β-sitosterol) was raised to 29-30%.

The precipitate which came down on cooling the mother liquor was collected and dried at 50°; yield 94 g aliphatic alcohols with m.p. 66-68° (25% on the crude phytosterol). After driving off the ethanol from the mother liquor, there was left 18-20% of solids with m.p. 80-90° and consisting of a mixture of aliphatic alcohols and sterols.

Quantitative determination of β-sitosterol

a) Determination of β-sitosterol with the help of dibromopyridine sulfate. 0.2-0.3 g exactly weighed β-sitosterol (dried at 100°) is placed in a flask with a ground glass stopper and dissolved in 15-20 ml chloroform; to the solution is added 15-20 ml of a solution of dibromopyridine sulfate. After 5 minutes' shaking, the contents of the flask should be transparent and yellow in color. In the event of turbidity a few milliliters of glacial acetic acid should be added until the solution clears (the excess of halogen amounts to 25-30% of the theoretically required amount). Back-titration is carried out with 0.1 N sodium thiosulfate solution after addition of 15 ml 10% potassium iodide solution, 50 ml water and 5 ml 0.5% starch solution (a blank is run in parallel).

Calculation is performed with the formula:

$$X = \frac{(a-b) \cdot 0.007992 \cdot 100}{c},$$

where X is the bromine number, a is the number of milliliters of 0.1 N dibromopyridine sulfate solution, b is the number of milliliters of 0.1 N sodium thiosulfate solution, and c is the weight of substance in grams.

The solution of dibromopyridine sulfate is prepared as follows: 8 g pyridine and 10 g sulfuric acid (d 1.84) were dissolved separately, each in 20 ml glacial acetic acid, and to the mixture was added 8 g bromine dissolved in 20 ml glacial acetic acid; the final solution was made up to 1 liter with glacial acetic acid.

The method for quantitative determination of β-sitosterol was tested on samples prepared by saponification of β-sitosterol-3-benzoate and twice recrystallized from ethanol. The date obtained are set forth in Table 1.

TABLE 1

Determination of Bromine Number of β-Sitosterol with the help of Dibromopyridine Sulfate

c	a − b	X
0.1470	7.10	38.6
0.2210	10.70	38.6
0.1438	7.02	38.8
0.2594	12.48	38.5

TABLE 2

Determination of Bromine Number of β-Sitosterol by the Bromide-Bromate Method

c	a − b	X
0.4190	19.99	38.13
0.3998	19.18	38.32
0.4668	22.48	38.49
0.3744	18.11	38.57

b) Determination of β-sitosterol by the bromide-bromate method. 0.3-0.5 g β-sitosterol (exactly weighed and dried at 100°) is placed in a flask with a ground-glass stopper; it is dissolved in 15 ml chloroform and addition is made of 25-35 ml 0.1 N potassium bromate solution, 10 ml 10% HCl and 1 g potassium bromide. After 15-20 minutes, addition is made of 20 ml 10% potassium iodide solution; the liberated iodine is titrated with 0.1 N sodium thiosulfate solution in presence of 5 ml 0.5% starch solution. A blank is run at the same time. Reaction temperature 6-9°.

In Table 2 are set forth the results of analysis of β-sitosterol prepared by saponification of β-sitosterol 3-benzoate.

The date of Tables 1 and 2 show that the results are perfectly satisfactory. (Thecalculated theoretical bromine number of β-sitosterol is 38.57.)

SUMMARY

1. A method is developed for the separation of β-sitosterol from vegetable sterols (phytosterol) based on extraction of the sterols with dichloroethane and recrystallization from ethanol.

2. It is shown that β-sitosterol can be quantitatively determined with the help of dibromopyridine sulfate (dissolved in glacial acetic acid) or of the bromide-bromate method.

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THE STRUCTURE OF SULFONIC ACIDS OF 2-AMINO-4-METHYLTHIAZOLE

II. CLARIFICATION OF THE STRUCTURE OF THE SULFONIC ACIDS OF 2-AMINO-4-METHYLTHIAZOLE WITH THE HELP OF INFRARED SPECTRA

S.G. Bogomolov, Yu.N. Sheinker and I.Ya. Postovsky

Depending on the reaction conditions the sulfonation of 2-amino-4-methylthiazole [1] may yield two isomeric sulfonic acids: a low-melting (m.p. 256°) and a high-melting one (m.p. 360° with decomp.), the low-melting isomer changing into the other when heated with sulfuric acid.

The problem of the structure of these acids and their respective derivatives had been a debatable one until recently. In most papers [2-4] the authors arrived at the conclusion that the low-melting acid is the sulfamic acid of 2-amino-4-methylthiazole and the high-melting acid is 2-amino-4-methylthiazole-5-sulfonic acid.

In the preceding paper [5] fresh chemical facts were submitted which refuted the above conclusion. The new data indicated that the low-melting acid is the sulfonic acid (the product of chlorosulfonation of 2-acetylamino-4-methylthiazole is the N-acetylated chloride of this acid), while the high-melting acid is evidently the sulfamic acid. In the light of these conclusions the transition of the low-melting into the high-melting acid is a rearrangement of sulfonic acid into sulfamic acid, and represents the first observed case of a transition of this type, which is opposite in character to analogous transformations in the series of aniline derivatives. For this reason, we considered it necessary to obtain supplementary evidence of the structure of these compounds, using not chemical, but physical methods, and particularly the method of infrared spectroscopy. On the basis of a study of the infrared absorption spectra of the isomeric sulfonic acids of 2-amino-4-methylthiazole and of a series of other derivatives of 2-aminothiazole, we have now obtained confirmation of the conclusions reached in the preceding paper [5].

EXPERIMENTAL

The infrared spectra of the 16 compounds listed in the table were plotted. For some of the compounds in the table the position of some substituted groups or atoms in the molecules is not indicated since their position was the subject of the present research.

All the substances were first repeatedly recrystallized until their melting points were constant.

Infrared absorption spectra in the 2 to 12.5 μ region were plotted with the help of an ISP 14^b infrared spectrometer with a NaCl prism. The apparatus was equipped with a simple mechanism permitting practically simultaneous regulation of the position of the zero point on the photogram, the transmissibility of air and the transmissibility of the sample of the investigated substance. For compensation of the drop in intensity of the source of radiation (carborundum rod) the width of the inlet and outlet slits during operation was automatically increased from 0.1 to 1 mm.

In addition to the apparatus with NaCl prism, the 2 to 3.5 μ region was measured with a spectrometer equipped with a LiF prism* which has a greater dispersion in this region.

Since nearly all of the investigated substances were distinguished by extremely poor solubility in solvents applicable for infra red spectroscopic work, the substances were investigated in the solid crystalline form in suspension in petroleum jelly.

The absorption spectra of all the investigated substances are represented in the diagrams on which the abscissas are wave-lengths in μ (or wave number in cm^{-1} and the ordinates are percentage transmissions. Absorption bands originating from the petroleum jelly are indicated in the diagrams by letter M.

Evaluation of Results

The solution in this investigation of the problem of the structure of the sulfonic acids of 2-amino-4-methylthiazole and some of their derivatives is founded on consideration of the data for absorption by these compounds of radiation in the spectral region of 3000-3700 cm^{-1} (3.3-2.6 μ). This region contains characteristic absorption bands of the NH groups (likewise OH); depending upon the nature of these groups (e.g. whether NH or NH_2)

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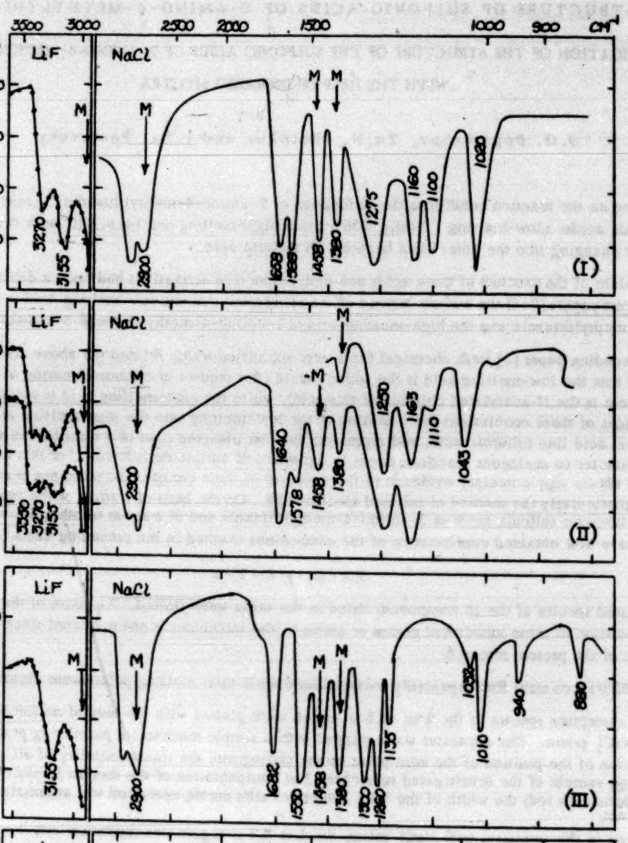
*The possibility of effecting measurements with an apparatus containing a LiF prism was kindly suggested to us by D.N. Shigorin, to whom the authors convey their thanks.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3000
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CM⁻¹
%
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60
40
20
LiF
NaCl
M
3270
3155
2900
1688
1588
1458
1380
1275
1160
1100
1020
(I)
LiF
NaCl
M
3330
3270
3155
2900
1640
1578
1458
1380
1250
1163
1110
1043
(II)
LiF
NaCl
M
3155
2900
1682
1550
1458
1380
1300
1260
1135
1032
1010
940
880
(III)
LiF
NaCl
M
3155
2900
1688
1551
1458
1380
1300
1225
1180
1080
1010
935
(IV)
2.86
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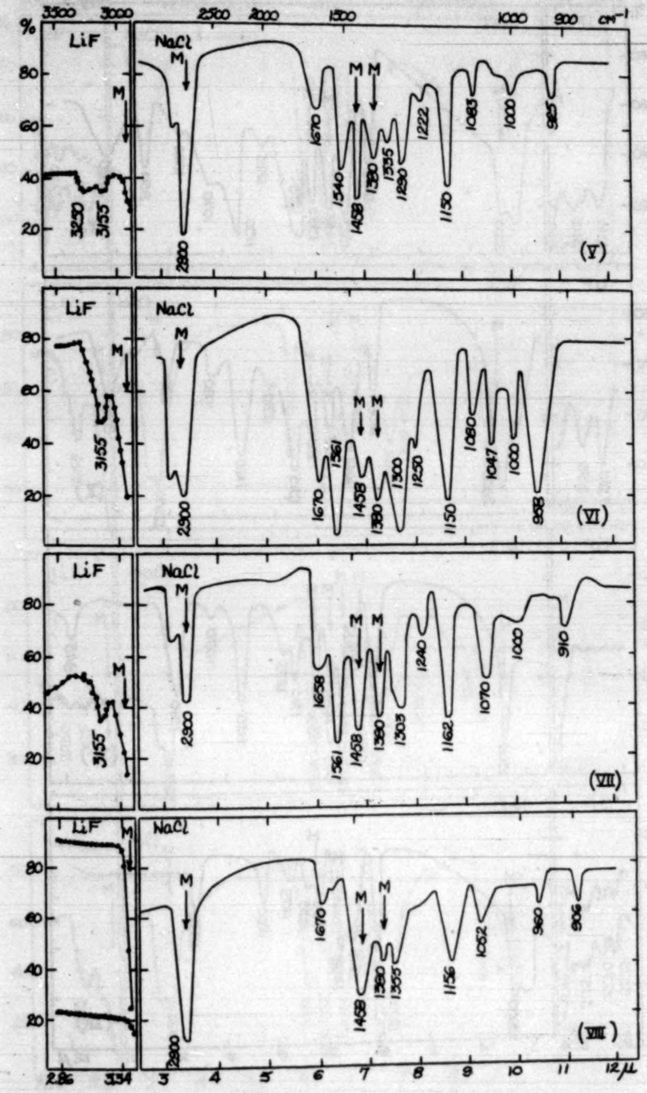
6
7
8
9
10
11
12 μ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M
M
M
3250
3155
2900
1670
1540
1458
1380
1335
1290
1222
1150
1083
1000
925
(V)
LiF
NaCl
M
M
M
3155
2900
1670
1561
1458
1380
1300
1250
1150
1080
1047
1000
958
(VI)
LiF
NaCl
M
M
M
3155
2900
1658
1561
1458
1380
1303
1240
1162
1070
1000
910
(VII)
LiF
M
NaCl
M
M
M
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1670
1458
1380
1355
1156
1052
960
906
(VIII)
2.86
3.34
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6
7
8
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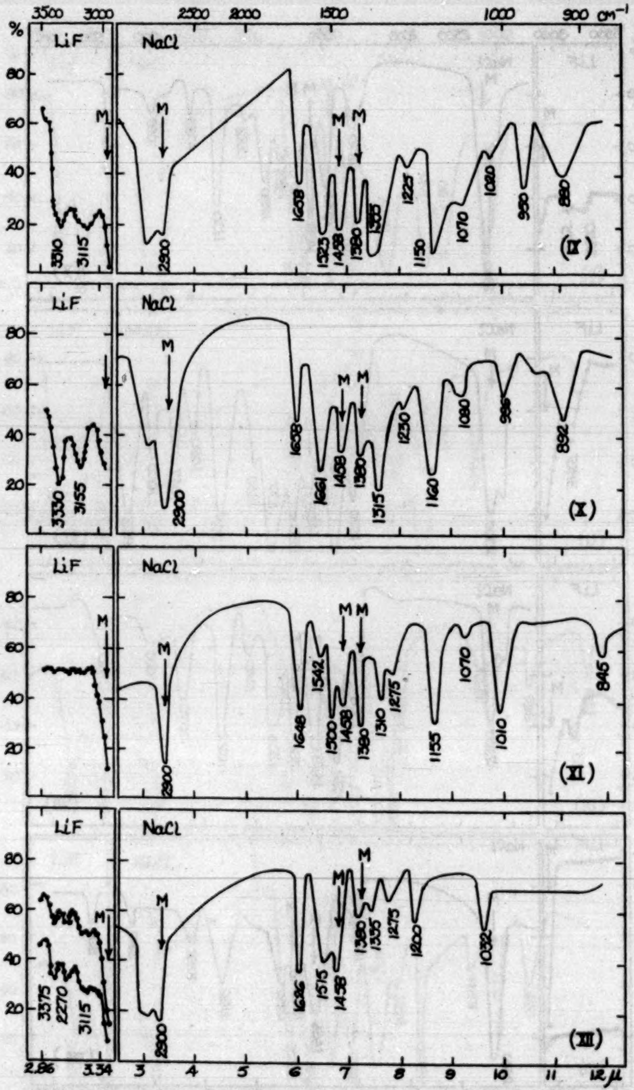
10
11
12 μ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%
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20
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3115
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1225
1150
1070
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950
880
(IX)
LiF
NaCl
M
3330
3155
2300
1658
1561
1458
1380
1315
1230
1160
1080
986
892
(X)
LiF
NaCl
M
2300
1648
1542
1500
1458
1380
1310
1275
1155
1070
1010
845
(XI)
LiF
NaCl
M
3375
2270
3115
2300
1626
1515
1458
1380
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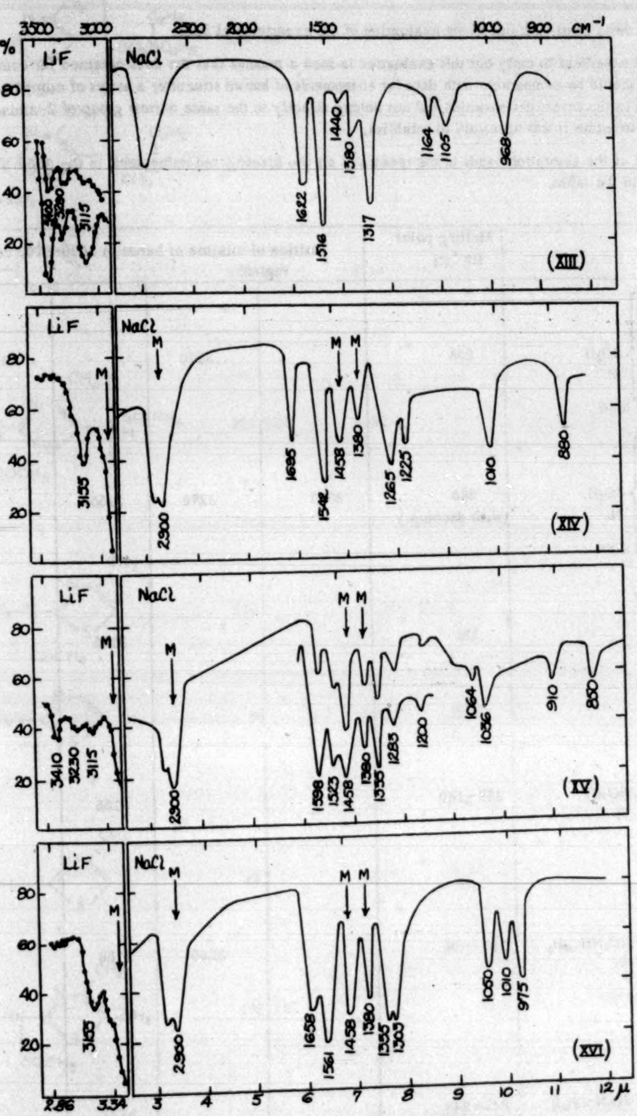
1032
(XII)
2.86 3.34 3 4 5 6 7 8 9 10 11 12 μ


3500
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CM⁻¹
%
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NaCl
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3230
3115
1622
1516
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1380
1317
1164
1105
968
(XIII)
M
3155
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1685
1542
1458
1380
1265
1225
1010
880
(XIV)
3410
3230
3115
2900
1598
1523
1458
1380
1335
1283
1200
1064
1036
910
850
(XV)
3155
2900
1658
1561
1458
1380
1335
1303
1050
1010
975
(XVI)
2.86
3.34
3
4
5
6
7
8
9
10
11
12 μ

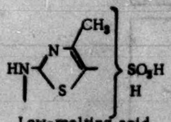
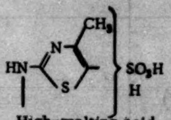
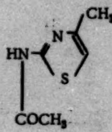
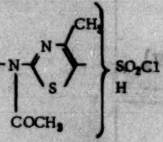
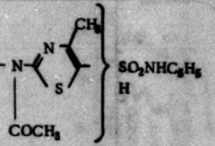
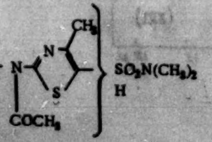
the system of characteristic bands in general will vary.

Complete absence of bands in this region is naturally due to the absence of such groups from the investigated molecules.

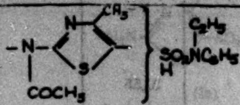
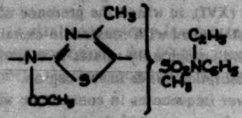
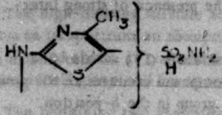
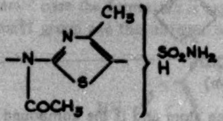
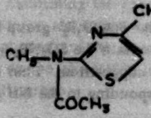
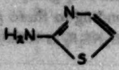
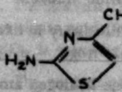
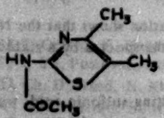
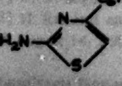
We applied these considerations to the evaluation of the experimental data.

It was found expedient to carry out this evaluation in such a manner that the data obtained for compounds of doubtful structure should be comparable with data for compounds of known structure; a series of compounds were therefore included in the investigation which did not belong directly to the same narrow group of 2-aminothiazole derivatives whose structure it was necessary to establish.

The position of the absorption bands in the spectra of all the investigated compounds in the 3000-3700 cm^{-1} region is set forth in the table.

Compound	Melting point (in °C)	Position of minima of bands in 3000-3700 cm^{-1} region			
(I)  Low-melting acid	256		3270		3115
(II)  High-melting acid	360 (with decomp.)	3350	3270	3155	
(III) 	132			3155	
(IV) 	159−160			3155	
(V) 	197−198		3250	3150	
(VI) 	242−243			3155	

(Continued on following page)

Compound	Melting point (in °C)	Position of minima of bands in 3000-3700 cm⁻¹ region			
(VII) 	188-189			3155	
(VIII) 	128-129	No absorption			
(IX) 	168-169	3310			3115
(X) 	225-226	3330		3155	
(XI) 	110	No absorption			
(XII) 	89	3375	3270		3115
(XIII)* 	42	3400	3290		3115
(XIV) 	146-147			3155	
(XV) 	149	3410	3230		3115

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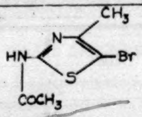
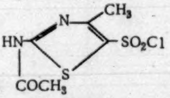
* The compound was investigated in the fused state.

(Continued)

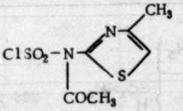
Compound	Melting point (in °)	Position of minima of bands in 3000-3700 cm^{-1} region				
	206				3155	

We see from the table that in the spectra of compounds (III), (XIV) and (XVI), in which the presence of one NH group is authenticated (the structure of these compounds was previously established with reasonable certainty [6,7], an absorption band in the 3155 cm^{-1} region is plainly visible. This band undoubtedly relates to vibration of the NH group since there are no other groups present which could possess absorption bands in this region. The considerable displacement of the band of the NH group in the direction of lower frequencies in comparison with the position of the band of the free NH group (3300 to 3400 cm^{-1}) testifies to the presence of strong intermolecular interaction in these compounds in the crystalline state.

In the spectrum of the product of sulfochlorination of 2-amino-4-methylthiazole (IV) we also find in this region an absorption band with a minimum at 3155 cm^{-1}. Consequently this compound contains an NH group and has the structure corresponding to formula (IVa), i.e. it contains the SO_2Cl group in the 5-position.



(IVa)



(IVb)

If the SO_2Cl groupwere present in this compound at the acetylated nitrogen atom and if the compound had the structure (IVb), then the band corresponding to the NH group should not be observable in the spectrum. Actually an absorption band is not observed in the spectra of compounds (VIII) and (XI) in which all the hydrogen atoms at the amino nitrogen are substituted (see the respective spectra).

Since the starting substance for the remaining investigated compounds containing the $SO_2NR_1R_2$ group is substance (IV), it may be thought that they all possess a similar structure, i.e. that they contain the $SO_2NR_1R_2$ group in the 5-position (R_1R_2 =H, Alk, Ar). The spectra of these compounds confirm this supposition. Thus the spectra of (V), (VI), (VII) and (X) have an absorption band in the 3155 cm^{-1} region corresponding to the NH group.

In the spectra of compounds (V) and (X) the presence in the $SO_2NR_1R_2$ radical of NH and NH_2 groups leads to the appearance in the 3000 to 3700 cm^{-1} region of supplementary absorption bands corresponding to these groups. In all these compounds, therefore, an NH group is present (at the amino nitrogen) and the $SO_2NR_1R_2$ is located in the 5-position.

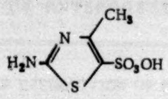
Substance (IV) (2-acetylamino-4-methylthiazole -5-sulfochloride) may be the starting substance for preparation of the low-melting sulfonic acid (I) which is formed from it by hydrolysis. Consequently the sulfo group in this compound must likewise be in the 5-position, while 2 hydrogens are linked to the amino nitrogen.

For the purpose of obtaining spectral confirmation of this hypothesis we first found it necessary to examine the spectra of compounds in which an NH_2 group was present in the 2-position of the thiazole ring.

This was necessary because in all the compounds hitherto considered not more than one hydrogen atom was present at the nitrogen in the 2-position. At the same time the sulfonic acid (if the above supposition is correct) must contain a NH_2 group whose absorption bands must differ from the absorption bands of the NH group.

Spectra of the compounds (XII), (XIII) and (XV) were plotted, and their examination shows that the NH_2 group in the 2-position of the thiazole ring (in the crystalline state) is represented in the spectra by a stable band at 3115 cm^{-1} and by two less stable bands at 3270 and 3400 cm^{-1}.

On comparing the spectra of these compounds with the spectrum of the low-melting sulfonic acid, we can see that the latter also contains absorption bands in the region of 3115 and 3270 cm^{-1}. Hence it follows that this compound contains a NH_2 group (and no NH which is characterized by a band at 3155 cm^{-1}), and that the structure of the low-melting acid corresponds to formula (Ia). Consequently the low-melting acid is 2-amino-4-methylthiazole-5-sulfonic acid, as also follows from the chemical data [5].



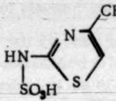
(Ia)

It is noteworthy that the spectrum of this compound is deficient in a third band, which is characteristic of the above-considered compounds containing NH_2 groups (3400 cm^{-1}), as well as in absorption bands in the 3300 to 3700 cm^{-1} region which should be assigned to vibrations of the OH group. It may be suggested that this is due to intermolecular interaction of the OH and NH groups which shifts the corresponding bands into the region of other observed bands (3300 to 3100 cm^{-1}).

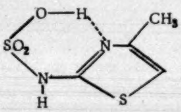
A similar spectrum is exhibited by compound (IX), prepared from (IV) by the action of ammonia. Due to the synthesis conditions, the SO_2NH_2 group must be in the 5-position and the NH_2 group in the 2-position, as in compound (I). In the spectrum of this compound (IX) are two bands at 3115 and 3300 cm^{-1} (as in the spectrum of the acid).

The high-melting sulfonic acid (II), obtained from the low-melting acid by heating with sulfuric acid, contains in its spectrum an absorption band at 3155 cm^{-1} as well as bands at 3270 and 3350 cm^{-1}. The 3155 cm^{-1} band, as noted above, is characteristic of the NH group in the compounds in question. Consequently this compound contains an NH group and has structure (IIa), i.e. it is 4-methylthiazole-2-sulfamic acid.

The remaining two absorption bands of this compound in the region considered are, in our opinion, associated with vibrations of the OH group which must participate both in intermolecular and intramolecular interaction. In the latter case the formation is extremely probable of an intramolecular hydrogen bond between the oxygen of the hydroxyl group and the nitrogen of the thiazole ring in the 3-position (IIb).



(IIa)



(IIb)

Examining the spectra in the region of lower frequencies, we may note that all the compounds exhibit two intense absorption bands at approximately 1550 to 1650 cm^{-1} which, judging by the literature data [8], are characteristic of the thiazole ring. Evidently in a series of compounds there is superposition of the above-noted bands on the absorption bands associated with the CO group of the acetyl radical or with deformed vibrations of the NH_2 group.

An intense absorption band in the 1150-1160 cm^{-1} region is observed for compounds whose molecules contain an SO_2 group. This absorption band evidently relates to the symmetrical vibration of the SO_2 group. According to the literature [9] this vibration has a value of 1150 cm^{-1} in sulfones.

SUMMARY

Consideration of the infrared spectra of the investigated compounds leads to the following conclusions.

1. The low-melting acid obtained by sulfonation of 2-amino-4-methylthiazole is 2-amino-4-methylthiazole-5-sulfonic acid (Ia), and the isomeric high-melting acid, formed from the low-melting acid by heating with H_2SO_4, is 4-methylthiazole-2-sulfamic acid (IIa).

2. The product of chlorosulfonation of 2-acetamino-4-methylthiazole is the N-acetylated acid chloride of the 5-sulfonic acid, and all the sulfamides obtained from the acid chloride are amides of this acid.

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[4] Ch. D. Hurd, H. Wehrmaster, J. Am. Chem. Soc., 71, 4008 (1949).
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[8] H. Randall and coworkers. Infrared determination of organic structures (1950).

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All-Union Scientific Research Institute of Pharmaceutical Chemistry, Moscow

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* See Consultants Bureau Translation, p. 1863.

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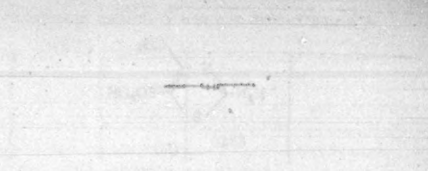

[illegible]

The high-intensity [illegible] (IV), [illegible] from the [illegible] contains in its spectrum an absorption band at [illegible] cm⁻¹ [illegible]

[illegible]

[illegible]

[illegible]

1. [illegible]

2. [illegible]

LITERATURE CITED

[1] [illegible]
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[3] [illegible]
[4] [illegible]
[5] I. Ya. Postovsky and [illegible]
[6] [illegible]
[7] [illegible]
[8] H. Rapoport and coworkers, [illegible]

Received August 15, 1960

All-Union Scientific Research Institute of [illegible]

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* See Consultants Bureau Translation, p. 1495.

MECHANISM OF HETEROGENEOUS CATALYTIC ISOMERIZATION OF HYDROCARBONS OVER ACIDIC CATALYSTS

I. MECHANISM OF INTERACTION OF PINENE, CAMPHENE AND LIMONENE WITH ISOMERIZATION CATALYSTS —TITANIUM DIOXIDE AND ACTIVATED CLAY

G. A. Rudakov, Z. S. Khomenko and M. M. Shestaeva

The catalytic isomerization of pinene over activated clays, discovered by Gurvich [1], has been studied by Tishchenko and Rudakov [2] who reached the conclusion that this catalyst behaves like an acid during the reaction. They based their conclusion both on the evidence in the literature about the acidic nature of clays [3, 4] and on the nature of the products which were obtained from pinene under the action of certain acids [5, 6].

The enunciated ideas about the role of the catalyst in the reaction were later widely accepted and were applied both to other hydrocarbons and other catalysts. Concerning, however, the mechanism of reaction of the liquid hydrocarbon with the solid catalyst, it has remained unclarified.

Tishchenko and Rudakov suggested that during the catalytic isomerization of pinene over activated clays, formation takes place, at the surface of the colloidal particles of aluminosilicic acids entering into the composition of clays, of unstable ethers which are susceptible to a series of rearrangements and whose breakdown results in products of isomerization of pinene — camphene and limonene.

During the past 20 years the ideas in question have undergone some modification, and recently a theory of the mechanism of isomerization of hydrocarbons over aluminosilicate and similar catalysts which has gained wide currency is based upon transformations of unstable carbonium ions which are formed by detachment of a proton from the catalyst and its addition to the unsaturated hydrocarbon [7, 8, 9]. An electron deficiency round one of the carbon atoms of the carbomium ion (sextet) is, according to this theory, the cause of the readily occurring rearrangement of the ion. Return of the proton to the catalyst or its transfer to another molecule of hydrocarbon after rearrangement of the cation leads to formation of a new isomer. A series of facts support the views enunciated about the mechanism of the reaction. These include the observations of Meerwein and coworkers [6, 10] on the ionic character of the retropinacoline rearrangement of the ether of isoborneol into the ether of camphene hydrate in a homogeneous medium, and the greater ease of understanding of the many processes from the standpoint of transformations of the carbonium ion. Unfortunately, the ionic concepts of the mechanism of heterogeneous isomerization of liquid hydrocarbons on acidic catalysts of the aluminosilicate type have been little developed, so that their value has been considerably reduced. While explaining some phenomena, these concepts lead to a series of problems which are not answered by the authors who have advanced the ionic mechanism of the reaction. Still unclarified is the state of the carbonium ions: are they, to any extent, free, like ions in solution, or are they all fixed to the surface of the catalyst, retaining on this surface the negative charges of the lattice as in the case of Ag^+ ions attached to the surface of AgCl particles? The assumption without special reservations of transfer of a protonfrom a carbonium ion to a hydrocarbon molecule with transformation of the latter into a new ion should, namely, lead to the assumption of the possibility of transfer of a proton from the surface to the space since the carbonium ion located at the surface of the catalyst is surrounded not only by molecules directly bordering on this surface. But if we assume the transfer of a proton into the space, we must also assume the presence during the reaction of a certain, if small, number of free ions in solution, and consequently we would be compelled to assume also the occurrence of a reaction outside the catalyst surface. In that event, the reaction, while starting at the catalyst surface, would continue in the course of a chain process outside this surface until the proton had been returned to the catalyst. The charge formed at the surface of the catalyst may, however, also be neutralized by other processes, for example the transfer of a proton to the catalyst by a molecule of hydrocarbon with simultaneous transformation into a carbonium ion. If transfer of a proton from the surface to the space is impossible, due for example to orientation of the carbonium ion by its positive charges toward the negative charges of the lattice, then proton transfer from the carbonium ion to the molecule bordering upon this ion at the catalyst surface must be of limited occurrence since the carbonium ion will be capable of transferring its proton only to that molecule which occupies the same position in relation to the anion of the lattice which it occupies itself.

The foregoing explanation of the mechanism of the reaction is extremely close to the explanantion given by Tishchenko and Rudakov. In both cases the formation is suggested at the catalyst surface of an intermediate compound – an ether; in both cases this intermediate compound is assumed to undergo rearrangement. But if we assert that the reaction involves rearrangement of the carbonium ion, this intermediate compound must be considered to be ionized. The concept of the ion in this explanation of the mechanism is similar to the concept of the ion in the crystal lattice or to the concept of the ion adsorbed by the lattice.

The investigations described below of the catalytic transformations of pinene, camphene and limonene on titanium dioxide and activated clay permit us to reach conclusions as to whether the reaction only proceeds at the catalyst surface or whether it is transferred to the space, while not touching upon the question of the ionic or non-ionic character of the reaction. Terpenes proved to be exceptionally convenient starting materials for this purpose since the lability of terpenes enabled the reaction to be conducted at relatively low temperature so that the reaction was not complicated by thermal transformations; moreover, as will be seen later, observations of isomeric transformations could be very conveniently made on the basis of changes of optical activity during the reaction.

As we know, the heating of α-pinene with active clays [2,11], titanium dioxide [12,13] and many other similarly acting catalysts results in its isomerization with formation of camphene, tricyclene, bornylene, fenchenes, limonene (dipentene), terpinolene and terpinenes. The main products of the reaction are camphene and monocyclic terpenes.

Isomerizing transformations of α-pinene are accompanied by changes of optical activity: the optical rotation of the mixture of reacting substances, i.e. a mixture of pinene and its transformation products rises during the first phase of the reaction, reaches a maximum before complete isomerization of the pinene, and then falls off rapidly (Figs. 1 and 1a).

The optical rotation of the reaction mixture rises at the start of the reaction because the α_D of the formed camphene and limonene is considerably higher than the α_D of the original pinene. The fall in optical rotation of the reaction mixture at the close of the reaction is due to various causes: in the reaction conditions the limonene may be transformed into terpinolene and terpinenes; also, as was established in the present investigation, the limonene may racemize; camphene also racemizes when heated with a catalyst due to reverse transformation into tricyclene [13] and possibly also to simultaneous rearrangement of the second order [14] which, as shown in the present investigation, may proceed with exceptional speed.

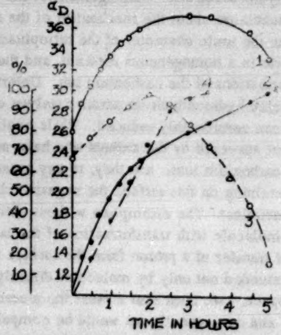

Fig. 1. Change of α_D of reaction mixture of terpenes during isomerization of pinene; 1) α_D of isomerizate obtained from pinene (sample 1, Table 1) when heated with 0.1% titanium dioxide at 60°; 2) % transformation of pinene (sample 1, Table 1) on heating with 0.1% titanium dioxide at 160°; 3) α_D of isomerizate obtained from pinene (sample 2, Table 1) on heating with 1% activated clay at 125°; 4) % transformation of pinene (sample 2, Table 1) when heated with 1% activated clay at 125°.

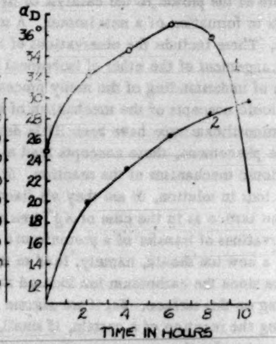

Fig. 1a. Change of α_D of reaction mixture of pinenes during isomerization of pinene 1) α_D of isomerizate obtained from pinene (sample 3, Table 1) on heating with 0.5% titanium dioxide at 135°; 2) % transformation of pinene.

It might be thought that the formation of camphene and limonene from pinene and their racemization proceed simultaneously and independently of one another. The rise of optical rotation during the first phase could then be regarded as the result of more rapid accumulation of products of of pinene), while the fall of optical rotation during the second phase may be regarded as the result of more rapid racemization of the products of reaction, coupled with their increasing concentration and the fall of concentration of pinene.

Careful analysis of the phenomenon compelled us to reject the foregoing hypothesis. On the basis of measurements of the α_D of the reaction mixture comprising pinene and the products of its isomerization obtained at different intervals during the reaction, and from determinations of the pinene content in this mixture effected at the instant of measurement of the α_D, it was possible to calculate the α_D of the mixture of substances formed from pinene at different instants of the reaction. It was found that the α_D of the products of isomerization remains constant as long as pinene is present in the reaction mixture in concentration not below 25-35%; only subsequently does rapid racemization of these products supervene (Figs. 2 and 3).

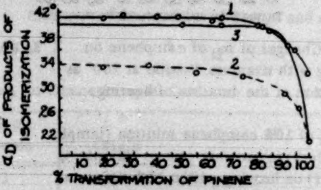

Fig.2. Change of α_D of products of isomerization as a function of the percentage transformation of pinene. 1) α_D of products of isomerization obtained from pinene (sample 1, Table 1) on heating with 0.1% titanium dioxide at 160°; 2) α_D of products of isomerization obtained from pinene (sample 2, Table 1) on heating with 1% activated clay at 125°; 3) α_D of products of isomerization obtained from pinene (sample 3, Table 1) on heating with 0.5% titanium dioxide at 135°.

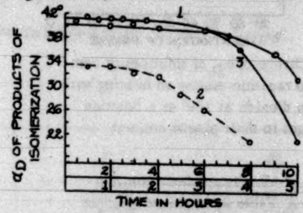

Fig.3. Change of α_D of products of isomerization of pinene as a function of the duration of the reaction.

1) α_D of products of isomerization obtained from pinene (sample 1, Table 1) on heating with 0.1 % titanium dioxide at 160°; 2) α_D of products of isomerization obtained from pinene (sample 2, Table 1) on heating with 1% activated clay at 125°; 3) α_D of products of isomerization obtained from pinene (sample 3, Table 1) on heating with 0.5% titanium dioxide at 135°. For 1 and 2 the duration is plotted on the lower scale; for 3 it is plotted on the upper scale.

The results obtained led to the conclusion that the catalyst begins to act upon the products of isomerization of pinene only after the main bulk of the pinene has reacted. In order to verify this conclusion experiments were carried out during which optically active camphene and limonene, dissolved in optically inactive pinene, were heated with titanium dioxide. The results of these experiments, plotted in Figs. 4 to 7, fully confirm this conclusion: both camphene and limonene, when dissolved in racemic pinene, retain their optical rotation when heated with the catalyst as long as the pinene concentration does not drop below a certain level. Inspection of the curves of change of α_D as a function of the duration of reaction (Figs. 3, 5 and 7) indicates that the activity of the catalyst gradually falls off during the reaction due to poisoning; therefore, the drop in α_D at the end of the reaction is less steep than it would have been if the catalyst had retained constant activity. A noteworthy feature is a certain difference between the behavior of optically active camphene and limonene, dissolved in racemic pinene, when heated with titanium dioxide at 160°. The start of racemization of limonene occurs at a concentration of residual pinene in the solution of about 30%, and racemization subsequently proceeds fairly quickly. Racemization of camphene on the other hand starts at a concentration of the residual pinene of about 50% but proceeds slowly in contrast to the extremely rapid racemization of pure camphene when heated with the same catalyst (Fig.5). It is interesting that camphene formed in the process of isomerization of pinene by titanium dioxide starts to racemize later, at a concentration of pinene in the reaction mixture of about 30% (Fig.2). From these data, obtained with two samples of camphene of different origins, we can conclude that racemization of camphene is retarded or even stopped because of the presence not only of pinene in the mixture but also of products of its isomerization, probably monocyclic terpenes or fenchenes. This is in agreement with existing data for the considerably stronger action of the catalyst upon fenchenes than upon camphene [11].

The very slight differences in behavior of camphene and limonene, dissolved in optically inactive pinene, when heated with titanium dioxide do not, however, alter the general picture of the process.

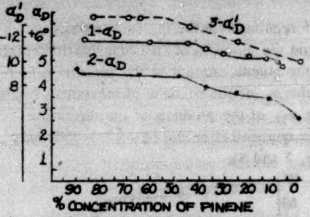

Fig.4. Change of α_D of solutions of camphene in racemic pinene on heating with titanium dioxide at 160° as a function of changes in their pinene content

1) α_D of 12.5% camphene solution (sample 2, Table 2) in pinene (sample 4, Table 1) on heating with 0.1% titanium dioxide; 2) α_D of 10% solution of camphene (sample 2, Table 2) in pinene (sample 4, Table 1) on heating with 0.15% titanium dioxide; 3) α_D of 16.2% solution of camphene (sample 1, Table 2) in pinene (sample 5, Table 1) on heating with 0.2% titanium dioxide added in two portions (0.1% at the start of the reaction and 0.1% at a concentration of the residual pinene of 65%).

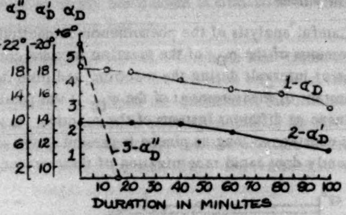

Fig.5. Changes of α_D of camphene on heating with titanium dioxide at 160° as a function of the duration of heating.

1) α_D of 10% camphene solution (sample 2, Table 2) in racemic pinene (sample 4, Table 1) on heating with 0.15% titanium dioxide; 2) α_D of 16.2% camphene solution (sample 1, Table 2) in racemic pinene (sample 5, Table 1) on heating with 0.2% titanium dioxide added in two installments (0.1% at the start of the reaction and 0.1% 40 minutes after the start of the reaction); 3) α_D of camphene (sample 3, Table 2) on heating with 0.1% titanium dioxide in absence of pinene.

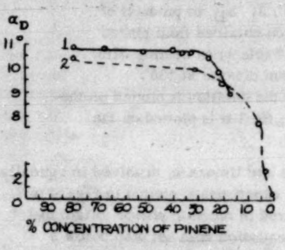

Fig.6. Change of α_D of a solution of limonene in racemic pinene on heating with titanium dioxide at 160° as a function of the changes of their pinene content.

1) α_D of 20% solution of limonene in pinene (sample 4, Table 1) on heating with 0.1% titanium dioxide; 2) the same with 0.2% titanium dioxide.

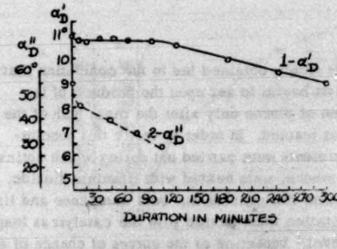

Fig.7. Changes of α_D of limonene in racemic pinene on heating with titanium dioxide at 160° as a function of the duration of heating.

1) α_D of solution of limonene in racemic pinene (sample 4, Table 1) on heating with 0.1% titanium dioxide;
2) α_D of limonene on heating with 0.1% titanium dioxide in absence of pinene.

The described course of the reaction is reliable evidence that the reaction takes place only at the surface of the catalyst. If the reaction had taken place in the space, it would have been difficult to explain why only a proton of a molecule of pinene should have been obtained in the space and not protons of the molecules of limonene and camphene present in solution together with the pinene and which rapidly racemize in the absence of pinene. On the other hand, if we assume that the reaction proceeds only at the surface of the catalyst and that at the reaction temperature the pinene is selectively adsorbed on this surface, the described course of the reaction becomes perfectly intelligible.

EXPERIMENTAL

1. Starting materials

The catalysts – titanium dioxide and activated clay – used in the investigation were prepared by the usual methods [2,12]; in order to ensure results which would be as comparable as possible, the catalysts used were all prepared by one method.

Constants of the samples of pinene and camphene used in the investigation are set forth in Table 1.

TABLE 1

Data for Pinene Samples Used

No. of sample	Origin	α_D	n^{20}_D	d^{20}_4
1	from oil of turpentine	26.05°	1.4654	0.8580
2	" " " "	23.30	1.4654	0.8581
3	" " " "	24.90	1.4660	-
4	obtained by mixing d and l-pinene* (ex-turpentine)	0.02	1.4653	0.8578
5	obtained via the nitrosochloride [16]	0.46	1.4654	0.8572

TABLE 2

Data for the Samples of Camphene Used

No. of sample	Origin	Solidification temp. (in °)	$[\alpha]_D$ in benzene (c = 50%)	n^{54}_D	d^{54}_4	MR_D
1	from fir oil	46	−102.5°	1.4560	0.8398	44.09
2	obtained by isomerization of pinene	47.5	+55.5	1.4759	0.8508	44.03
3	obtained by isomerization of pinene	48	+22.3	1.4538	0.8437	43.70**

Limonene was isolated from the products of isomerization of pinene effected in presence of titanium dioxide as catalyst. Physical properties of limonene:

n^{20}_D 1.4729; α^{20}_4 0.8419; MR_D 45.35; calc. 45.24; α_D 54.78°; $[\alpha]_D$ 65°.

The individaul terpenes were isolated with the aid of the efficient rectifying columns previously described [15].

2. Isomerization of the terpenes

Isomerization of terpenes was carried out in a three-necked round-bottomed flask fitted with reflux condenser, thermometer and motor-driven stirrer. The amount of terpenes in individual experiments varied between 40 and 200 ml. In order to avoid poisoning of the catalyst by products of oxidation, the terpenes were used in the freshly distilled condition and 0.01% hydroquinone was added as inhibitor. The catalyst was added when a temperature 100° had been reached, and from the instant of attainment of a temperature 5° below the required one, the reckoning of duration and the periodic withdrawal of samples was started. The mixture was heated as rapidly as possible. In many cases the reaction temperature was governed by the boiling point of the mixture. In the case of isomerization of pinene, the mixture boiled at 155°, but due to the rapid accumulation of reaction products the boiling point quickly rose to 160°. Withdrawal of samples in the course of the process was effected with a pipet through the reflux condenser. The samples were filtered before determinations were carried out of their camphene content and α_D. The camphene content was determined by the formylation method

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* We extend our best thanks to I. I. Bardyshev, who placed this sample at our disposal.

** Sample contains tricyclene as impurity.

[17] with introduction of a correction for incompleteness of the reaction (94%). Other terpenes which react with formic acid were analyzed by this method: tricyclene, bornylene and fenchenes. Employment for the polarimetric determinations of a tube 50 mm long and 2 mm in diameter in conjunction with the camphene determination enabled us to use samples of 2 g and even less.

3. Calculation of optical rotation of the products of isomerization

Unreacted pinene was also present in samples of isomerizate withdrawn in the course of the process and consisting mainly of camphene and limonene.

The additivity of the properties of solutions of terpenic hydrocarbons was taken into account in the calculation of the optical rotation of the products of isomerization contained in each sample, applying the following formula:

$$\frac{\alpha'_D \cdot n'}{100} + \frac{\alpha''_D : n''}{100} = \alpha_D, \tag{1}$$

hence

$$\alpha''_D = \frac{100 \cdot \alpha_D}{n''} - \frac{\alpha'_D \cdot n'}{n''}, \tag{2}$$

where α_D is the optical rotation of the reaction mixture, α'_D is the optical rotation of the original pinene, α''_D is the required optical rotation of the products of isomerization, n' is the percentage of pinene in the reaction mixture, n'' is the percentage of products of isomerization in the reaction mixture. α_D and α'_D can be easily measured, while n' and n'' are mutually dependent since

$$n'' = 100 - n', \tag{3}$$

and hence for the calculation of α''_D it suffices to know n' or n''. Since direct determination of n' or n'' consumes much time and a large amount of substance, determinations were made on the basis of indirect calculation from the readily determinable content of camphene in the samples (by the formylation method) according to the formula:

$$\frac{a}{b} \cdot 100 = n'', \tag{4}$$

where a is the percentage of camphene in the sample concerned, b is the percentage of camphene in the isomerizate at the instant of complete transformation of the pinene. Under the action of a mixture of HCOOH and H_2SO_4 in the reaction conditions, pinene is transformed to the extent of 10% on the average into an ether which results in too-high results for n'' when calculated according to formula (4) and correspondingly to too-low results for n'; a correction in accordance with formula (5) is, therefore, introduced into the values of n' calculated from formulas (3) and (4):

$$n'_{\text{corr.}} = n' + 0.099n' \cdot c^{-1} + 0.012n' \cdot c^{-2}, \tag{5}$$

where

$$c = \frac{b}{100}.$$

4. Establishment of racemization of limonene when heated with titanium dioxide

The starting product used in the investigation was an isomerizate with α_D 10.4°, n_D^{20} 1.4812, obtained from limonene by heating with 0.1% titanium dioxide for 3 hours; it contained 96% monoterpenes and 4% polymers. The monoterpenes (54 g) contained in the isomerizate, separated from polmers by vacuum-distillation of the isomerizate, were subjected to rectification, the results of which are plotted in Figure 8. The fractionation curves enable the fractions to be arranged in 5 groups denoted by the letters A to F.

Group A (2.8%, fraction 1 – n_D^{20} 1.4732; d_4^{20} 0.8504; α_D 8.72°) consists of an unidentified component present in admixture with monocyclic terpenes.

Group B (18.5%, fractions 2 to 8). The characteristic fraction of this group is fraction 6 (n_D^{20} 1.4768; d_4^{20} 0.8414; α_D 14.0°; b.p.173°). In the mixture of fractions of group B were found terpinene (nitrosite with m.p. 155°) and limonene which was isolated, after removal of α-terpinene, in the form of an adduct with maleic anhydride. For this purpose 1 g maleic anhydride was added to 5 g of the mixture of fractions in 5 ml anhydrous ether. After 48 hours the product was washed with 4% NaOH solution and after removal of the ether it was distilled in vacuum. The distilled limonene had the following constants: n_D^{20} 1.4749; d_D^{20} 0.8443; α_D 24.36°; tetrabromide of the dl-form, m.p. 125°.

Group C (15.5%, fractions 9 to 13) was regarded as an intermediate group and was not examined.

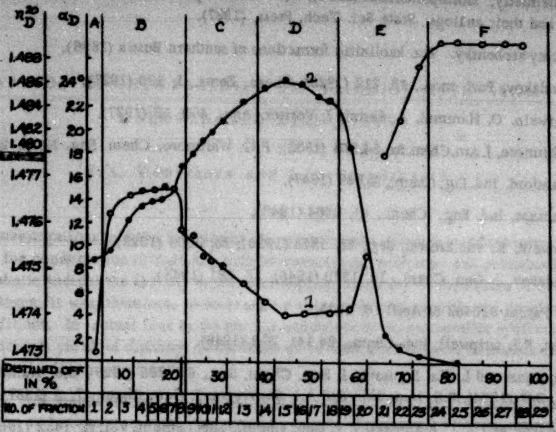

Fig.8. Results of rectification of products of isomerization of limonene.

1) n_D^{20}, 2) α_D.

Group D (17.4%, fractions 14 to 18) consists to a considerable extent of racemized limonene. All the fractions of this group were combined and treated with maleic anhydride. The limonene isolated after this treatment had the following constants which nearly coincided with those of the best 15th fraction: n_D^{20} 0.8436; α_D 24.8°; b.p. 175.5°; tetrabromide, m.p. 125°.

Group E (20.5%, fractions 19 to 23) may be regarded as intermediate between the limonene and terpinolene groups but apparently contains also γ-terpinene although we failed to obtain derivatives of the latter. Fraction 20, characteristic of Group E had the following properties: n_D^{20} 1.4759; d_4^{20} 0.8453; α_D 9.5°; b.p. 178°.

Group F (26.3%, fractions 24 to 29) consists mainly of terpinolene. The characteristic 26th fraction had the following constants: n_D^{20} 1.4906; d_4^{20} 0.8637; MR_D 45.7; calcd. 45.7, taking into account the hemicyclic position of the double bond; terabromide, m.p. 117°.

The foregoing data conclusively point to racemization of the limonene (fall in α_D from 54.78 to 24.8°).

Approximate composition of the isomerizate: limonene and dipentene 42, terpinolene 35, terpinenes 19, polymers 4%.

SUMMARY

1. Although pinene, camphene and limonene – separately – rapidly isomerize, while they also racemize when heated with titanium dioxide, camphene and limonene do not suffer any change when they are heated with the same catalyst in presence of pinene.

2. Catalytic isomerization of pinene over activated clay at 125° and over titanium dioxide at 135-160° leads to formation of camphene and limonene which resist the action of these catalysts until the pinene concentration in the reaction mixture falls to 25-35%.

3. The foregoing phenomena are due to reaction only taking place at the catalyst surface of the selectively adsorbed pinene and not in the liquid. This fact has general significance for the understanding of the mechanism of heterogeneous isomeric transformations of liquid hydrocarbons over catalysts like aluminosilicates and titanium dioxide.

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CONDENSATION OF PHENYLALUMINUM DIIODIDE WITH AROMATIC HALOGENATED DERIVATIVES

E.A. Vdovtsova and I.P. Tsukervanik

Continuing our investigations into the reaction of phenylaluminum diiodide with halogenated derivatives [1,2], we have studied the condensation of $C_6H_5AlI_2$ with bromobenzene, p-chloro- and p-bromotoluenes. It was observed that with aliphatic iodides the facility of reaction depends markedly on the nature of the radical and the mobility of the halogen; it was, therefore, to be expected that condensations with aryl halides would only proceed in drastic conditions. In actual fact in the normal conditions of organometallic synthesis no reaction occurs: in these experiments yields of diphenyl of the order of 10-15% are due to its formation in the process of preparation of the organoaluminum compound.

Organoaluminum compounds are not exceptional in this respect. Phenyl derivatives of other, more active, metals – sodium, lithium and magnesium – in their reaction with halobenzenes [3] likewise give low yields of diphenyl (15-20%). Only in conditions facilitating the dissociation of C_6H_5Me into radicals is it possible to obtain yields of diphenyl close to the theoretical, for example in the condensation of phenylmagnesium bromide with bromobenzene in presence of $CoCl_2$ [4] or, as our investigations showed [1], by conducting the synthesis in an autoclave at 150-200°.

In the case of $C_6H_5AlI_2$ we succeeded in obtaining at 245-255° diphenyl in a yield of over 90% of the theoretical by interaction with bromobenzene and in a yield up to 30% with p-chlorotoluene (Tables 1 and 2). The aluminum halide formed during the reaction energetically reacts with the condensation product and easily resinifies it [5]; the reaction, therefore, calls for relatively short-period contact of the reactants (30-60 minutes) and strict maintenance of the specified temperature range; complete charring takes place at above 260° or on prolonged heating.

Products, apart from diphenyl, which could be isolated in condensations with bromobenzene were terphenyl, quaterphenyl and quinquephenyl. A crystalline substance with m.p. 95.5-101.5° was also isolated; we suggest that it is p-dicyclohexylbenzene.

Optimum conditions could not be found for reactions with p-chloro- and p-bromotoluenes. The main bulk of the organoaluminum compound does not react (the reaction mixture decomposes with intense heat liberation). Here also diphenyl is the main product. Traces of terphenyl and an oily substance were also isolated. The fact that p-chloro- and p-bromotoluenes do not form methyldiphenyls suggests that in these reactions there is dimerization of the phenyl radicals formed on thermal dissociation of phenylaluminum diiodide:

$$2C_6H_5AlI_2 \xrightarrow{245-255^\circ} C_6H_5{-}C_6H_5 + 2[AlI_2]$$

In the absence of aryl halide, however, thermal dissociation does not take place in these conditions (expt. 4, Table 1) and the diphenyl yield is only 13%. This is in accord with our previously obtained data for the interaction of phenylmagnesium bromide with bromobenzene [1]. It may be suggested that the halogenated derivative is necessary for reduction of aluminum subhalide, as is the case in the organomagnesium synthesis in presence of $CoCl_2$ [4]:

$$C_6H_5Br + \cdot AlI_2 \rightarrow C_6H_5\cdot + AlI_2Br.$$

The free phenyl radical either enters into reaction with excess benzene or disproportionates to give polyphenyls [5, 6, 7]. The fate of the p-chlorophenyl radical could not yet be established.

EXPERIMENTAL

The mixture of components was heated in an autoclave. Conditions and results of condensations are set forth in Tables 1 and 2. Below is a description of an experiment giving maximum yields of diphenyl.

Condensation of phenylaluminum diiodide with bromobenzene (expt. 11). Into an autoclave of 100 ml capacity were charged, in a nitrogen atmosphere, 40 ml of a benzene solution (from 70 ml) of $C_6H_5AlI_2$ prepared from 42.8 g C_6H_5I and 4.2 g Al and 30 g bromobenzene [1]. The mixture was heated for an hour at 245-250°. After cooling, the autoclave was opened and the mass run into ice containing hydrochloric acid. The aqueous layer was repeatedly extracted with benzene. The very dark-colored (due to iodine) benzene extract was twice washed with water, with dilute caustic alkali, and again with water. Treatment with alkali caused separation

TABLE 1

Condensation of $C_6H_5AlI_2$ with bromobenzene (30 g)*

No. of expt.	$C_6H_5AlI_2$ from C_6H_5I (in g)	Duration of heating (in hours)	Temperature	C_6H_5Br recovered (in g)	Residue (in g)	Diphenyl	
						(in g)	(in %)
1	20.4	-	-	-	2.1	1.0	13.0
2	22.7	-	-	-	1.6	1.3	14.7
3	10.2	-	-	-	0.9	0.4	10.4
4	15.3	18.0	200-250°, towards the end 300	-	2.25	0.85	14.9
5	20.4	3.5	210-220, towards the end 250**	-	-	Traces	
6	21.7	1.0	220-230, towards the end 250	23.7	21	1.7	20.7
7	18.1	2.0	220-230**	18.6	7.0	4.4	64.7
8	20.4	6.0	220-240	-	-	0.5	6.5
9	16.3	2.0	220-240, towards the end 260	27.7	3.8	2.6	43.0
10	20.4	4.5	220-250, towards the end 260**	-	-	0.5	6.5
11	23.3	1.0	245-256	5.6	14.2	8.6	97.7
12	20.4	0.5	244-256	8.5	12.5	6.9	90.0
13	17.5	1.0	256, towards the end 270**	-	-	0.5	7.5
14	18.1	0.5	250-280***		Not worked up		
15	22.7	0.5	250-300***		Not worked up		
16	18.1		Rapidly to 300	26.5	5.5	3.5	45.4

TABLE 2

Condensation of $C_6H_5AlI_2$ with p-chloro- and p-bromotoluenes

No. of expt.	$C_6H_5AlI_2$ from C_6H_5I (in g)	ArX (in g)	Solvent	Duration of heating (in hours)	Temp.	ArX recovered (in g)	Residue (in g)	Diphenyl	
								(in g)	(in %)
1	16.8	32.1	p-Chlorotoluene	0.7	95-160°	27.0	1.3	0.8	15.7
2	20.4	32.1	Benzene	15.0	140-150	28.9	1.7	1.0	13.0
3	20.4	26.7	p-Chlorotoluene	11.5	170-180	16.0	2.1	1.1	14.3
4	20.4	32.1		14.5	200-205	20.3	-	2.0	26.0
5	20.4	26.7	Benzene	6.0	200-240, toward end 260	-	-	2.1	27.3
6	20.4	32.1	p-Chlorotoluene	10.0	240-260**	-	-	0.5	6.5
7	20.4	20.8*	Benzene	0.7	246-252	17.5	2.2	1.4	18.2
8	20.4	21.4	Benzene	0.8	248-252	14.5	3.8	2.3	30.0
9	20.4	12.8		0.75	250-258	9.9	2.5	1.7	22.1
10	20.4	21.4		0.5	244-252	-	2.0	1.5	19.4
11	20.4	20.8*		0.7	256-268**	-	1.2	1.1	14.3
12	20.4	20.8*		1.0	244-261**	-	0.6	0.4	5.2
13	21.3	32.1	p-Chlorotoluene	10.0	250-300***	-	-	-	-
14	20.4	16.0		13.0	300-320***	-	-	-	-

TABLE 1:

- * Experiments 1 to 4 without bromobenzene.
- ** Reaction product (resinous mass) steam-distilled.
- *** Complete charring of reaction products.

TABLE 2

- * Experiments performed with p-bromotoluene
- ** Reaction product (resinous mass) steam-distilled.
- *** Complete charring of reaction products.

of a brown precipitate which was filtered off. After drying with calcium chloride, the benzene was distilled off followed by the bromobenzene up to 200° (4 g recovered). The residue (14.2 g) was distilled in vacuum to give the following fractions (at 40 mm): 1) b.p. up to 110° (mixture of bromobenzene and diphenyl), 1.6 g; 2) b.p. 140-210°, 8.6 g. From the residue at 0.2 mm was obtained a crystalline fraction 3) with b.p. up to 360°, 0.6 g.

Refractionation of fractions 1) and 2) yielded crude diphenyl with b.p. 140-150° at 35 mm (6.4 g) and a substance with b.p. 140-145° at 4 mm (2.4 g). The diphenyl fraction was fractionally crystallized from ethanol. Diphenyl was isolated with m.p. 69.5-70° [8]; it did not give a melting point depression with an authentic specimen. A small amount of oil (a) was obtained. The fraction with b.p. 140-145° at 4 mm and m.p. 76-82° was crystallized from methanol. An oil b was obtained (which was mixed with oil a) and crystals with m.p. 89-90°. Their fractional crystallization from dilute ethanol gave a substance (A) with constant m.p. of 95.5-100° and a pleasant, orangey odor (presumably p-dicyclohexylbenzene).

Fractionation of oils a and b gave: diphenyl with b.p. 116-121° at 8 mm (0.7 g), substance (A) with b.p. 121-128° at 2 mm (0.8 g), an oil with b.p. 132-140° at 2 mm (0.6 g) and terphenyl mixed with oil with b.p. 160-200° at 2 mm (0.9 g).

The 3rd fraction with b.p. up to 360° at 2 mm was dissolved in a large excess of hot ethanol. Terphenyl with m.p. 199-201° came down on cooling. After sublimation and two recrystallizations from benzene the m.p. was 206-207° [8]. A mixed test with an authentic specimen of terphenyl does not give a melting point depression. A portion of the crystals, insoluble in ethanol, melts at 301°. The crystals which adhered to the condenser and the resin which remained in the flask were extracted with hot benzene; addition of ethanol, brought down a light-brown flocculent precipitate with m.p. 268°. Two sublimations gave white crystals with m.p. 288°. The mixture of high-melting crystals was digested with a 20-fold excess of benzene in order to remove the terphenyl. A substance with m.p. 317-318° was isolated which from the conditions of isolation and the melting point is identified as quaterphenyl [8].

The brown precipitate, filtered from the benzene extract of the condensation product, was sublimed to give quinquephenyl with m.p. 372°. The literature [7] reports 370° for the sublimed product and 388.5° after washing and recrystallization from quinoline.

The same products were obtained in expt. 12. Diphenyl with b.p. 104-110° at 5 mm (6.9 g).

Condensation of phenylaluminum diiodide with p-chlorotoluene (expt. 8). Reactants were a 40 ml benzene solution of $C_6H_5AlI_2$ (from 80 ml), prepared from 42.8 g C_6H_5I and 4.2 g Al, and 21.4 g p-chlorotoluene. The mixture was heated at 248-252° (mainly at 250°) for 50 minutes. Considerable heat is evolved when the reaction mixture is decomposed. 14.5 g p-chlorotoluene (up to 200°) was recovered. Fractionation of the residue (3.8 g) gave the following fractions: 1) b.p. up to 120° at 100 mm, 0.6 g; 2) b.p. 116-120° at 12 mm, 2.3 g (diphenyl); 3) b.p. 170-230° at 8 mm, 0.7 g (crystals mixed with oil). From the latter fraction was isolated terphenyl with m.p. 199-200°, not giving a depression of melting point with an authentic specimen.

SUMMARY

1. The condensation of phenylaluminum diiodide with bromobenzene, p-chlorotoluene and p-bromotoluene was studied.

2. Optimum conditions were found (heating in autoclave for an hour at 245-255°) for preparation of diphenyl in a yield of 90% of the theoretical from the reaction of $C_6H_5AlI_2$ with bromobenzene. By-products identified were terphenyl, quaterphenyl and quinquephenyl.

3. It was shown that the main product in condensations of $C_6H_5AlI_2$ with p-chloro- and p-bromotoluenes is diphenyl (up to 30% of the theoretical).

4. It is suggested that interaction of $C_6H_5AlI_2$ with aryl halides proceeds by a radical mechanism resulting from thermal dissociation of $C_6H_5AlI_2$.

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THE HYDROGEN BOND AND THE PHYSICAL PROPERTIES OF 8-HYDROXYQUINOLINE

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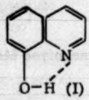
The presence of an intramolecular hydrogen bond in 8-hydroxyquinoline (I) is demonstrated by a series of properties: low area of molar absorption of the OH group in the infrared region [1], low acidity [2], facility of formation of inner-complex salts [3]. For the purpose of clarifying the influence of this type of bond on the physical properties of 8-hydroxyquinoline, determinations were made of density, surface tension and viscosity at 209° of 8-hydroxy- and 8-methoxyquinolines, also of the viscosity of quinoline (table). In the table are also set forth data for the boiling point of quinoline and some of its hydroxy and methoxy derivatives.


(I)

Physical Properties of Hydroxy- and Methoxyquinolines

Compound	Absolute b.p.	d_4^{209}	γ (209°)	$\eta \cdot 10^3$ (209°)
Quinoline	511	0.937[4]	24.7[4]	3.90
4-Hydroxyquinoline	573	–	–	–
6-Hydroxyquinoline	> 633	–	–	–
8-Hydroxyquinoline	540(752)	1.034	28.1	5.27
6-Methoxyquinoline	578(740	1.000	–	–
8-Methoxyquinoline	555(750)	1.012	28.0	6.04

It follows from the data obtained that formation of an ether from 8-hydroxyquinoline, as in the case of substituted phenols with a stable intramolecular hydrogen bond [5], brings about a rise of viscosity with rising boiling point and hardly any change in surface tension. Compared with its isomers, 8-hydroxyquinoline possesses a much lower boiling point (a similar difference was observed in the above-mentioned disubtituted benzenes), while its isomers possess – in contrast to 8-hydroxyquinoline – a much higher boiling point in comparison with their methyl ethers. Like o-nitrophenol in relation to nitrobenzene, 8-hydroxyquinoline exhibits a relatively small rise of the above constants over quinoline. In this connection, as is also characteristic of substituted benzenes with an intramolecular hydrogen bond [5], the relative rise of density on introduction of a hydroxyl into quinoline in the 8-position appreciably lags behind the relative rise of molecular weight (1.110 and 1.124 respectively).

Consequently the physical properties of 8-hydroxyquinoline are in harmony with the concept of the presence in its molecule of a stable hydrogen bond. The regularities established for substituted benzenes in respect of various physical properties of inter- and intramolecularly associated compounds prove to be applicable also to the correspoding heterocyclic compounds.

EXPERIMENTAL

Quinoline was purified by two distillations and collection of the 232° (754 mm) fraction. 8-Hydroxyquinoline, white needles with m.p. 75° was purified by distillation and recrystallization from ethanol-water mixture. 8-Methoxyquinoline [6] was prepared by methylation of 8-hydroxyquinoline with methyl iodide in methanol; it was purified by distillation, b.p. 281-282° (750 mm).

The procedures for determination of density, viscosity and surface tension have been described already [5]. The pycnometer and capillaries were calibrated against quinoline. The liquid used for establishment of a constant temperature in the vapor thermostat [7] was nitrobenzene.

SUMMARY

1. Determinations were made of the density, surface tension and viscosity at 209° of 8-hydroxy- and 8-methoxyquinolines.

2. It was shown that the regularities characteristic of the physical properties of substituted benzenes with an intramolecular hydrogen bond are also observed in the corresponding heterocyclic compounds.

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THE NUMBER OF LINEAR AND CYCLIC α-AMINOACID BONDS IN THE PROTEIN MOLECULE

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With reference to a whole series of examples we showed [1,2,8] the possible existence in the protein molecule of the following structures: amidine, N-amino-acylpiperazine, amidino-aminoacyl, and carbonnhydride. The synthesis and examination of the properties of these structures enable already the establishment of the principal valency bonds in the protein molecule, which abroad are regarded as linear anhydride bonds.

According to the polypeptide theory of proteins there exists a chain molecule whose length with bonds of the valency type is within the range of 300-20000 amino acids. The whole diversity of protein forms, on the hypothesis of a linear-anhydride structure, is explained by spiral coiling of this gigantic chain or to formation of diverse loops. The latter explanation, however, fails to account for the lability and other properties inherent in proteins.

In opposition to the above-mentioned theory, we suggest, on the basis of experiments, that protein is a polymer of a complex anhydride (monomer) built up from 5-8-16 amino acids. This polymer is formed by the joining together, with the help of supplementary valencies, of an integral number of molecules of the original low-molecular (M about 1000) micromolecule. It is not excluded that in this type of compounds there are present in equilibrium in a variety of states all the fragments of the micromolecule (monomers) that we obtained. Consequently the anhydride-polymer hypothesis advanced by one of us (N.I. Gavrilov) refutes the existence of the long polypeptide chain and reduces the polypeptide portion of the protein molecule to the size of three amino acids. Such a linear anhydride is linked to the cyclic anhydride, diketopiperazine, amidine and aminoacyl forms of linkage. The result is a linear-cyclic anhydride and a structural micromolecule is developed which further polymerizes into a macromolecule. The micromolecule is very active and capable of a number of transformations.

Kober [3] was the first to point out that the absorption curve of the copper complex of protein strongly resembles the absorption curve of a tripeptide. Jesserer and co-workers [4] attempted to characterize the structure of protein with the aid of "copper numbers". On the erroneous assumption that the "violet" protein complex, in their opinion, is obtained by mixing the "red" complex of the same protein with the blue color of the copper cation present in the complex, they could not utilize the biuret reaction for problems of protein structure.

The biuret reaction was again applied by Plekhan [5] to the elucidation of the structure of protein and with its aid were established all the regularities of the structure of the copper biuret complexes of peptides.

In this paper we attempt a quantitative comparison of the participation of tripeptides and diketopiperazines (Table 5) in the building up of the protein micromolecule. Our task was hindered by the presence in protein of a large number of prosthetic groups, sometimes of unknown structure. In proteins containing phosphoric or sulfuric acids (casein, sturin sulfate), glucosamine (albumin), and a small amount of carbohydrates (edestin, etc.), corrections for their quantity give very satisfactory results by comparison with experimental data and theory. We also found difficulty in establishing the number of amino acids in the large polymeric molecule and in connection with the inconstancy of its amino acid composition [6]. We succeeded, nevertheless, in making the desired comparison to a rough approximation in the case of a series of proteins, excluding gelatin.

For the quantitative content of cyclic forms of bonds in proteins we made use of data from papers by Koperine [2] and Ioanisiani [7] who used the electroreduction method. For all proteins with a known content of cyclic bonds we determined the "copper numbers"*, which for casein agreed with the value previously obtained by Plekhan [5].

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*Plekhan defines the copper number as the amount of protein in grams which binds 1 g-atom of copper to form the copper complex. A titrimetric method was also proposed for determination of copper numbers [5].

Into the "copper number" enters: 1) 1 mole protein tripeptide composed of three amino acids of average (for a given protein) molecular weight; 2) a corresponding proportion of diketropiperazine required for the three amino acids of the tripeptide. The amino acid weight of the diketopiperazine was calculated from the mean relative amount of amino acids entering into its composition, i.e. phenylalanine, proline, serine, and leucine, and partly from the corresponding amounts of alanine and glycine; 3) the mean weight of non-amino acid components of the given protein, i.e., sulfuric and phosphoric acids, carbohydrates and glucosamine recalculated to 3 + 2x amino acids (x being the proportion of diketopiperazine required for the tripeptide) and calculated according to their percentage ratio in the whole of the protein molecule.

For all proteins the calculated "copper numbers". allowing for the prosthetic groups, agreed in the majority of cases with the experimental values.

This agreement enables us to postulate: 1) The existence of the cyclic forms of bonds in the protein molecule; 2) the presence of three amino acid fragments in the peptide portion of the structure of the protein molecule.

In the present investigations we made no reference to the amidino-acyl forms of bond which we not only discovered in the case of model structures but also proposed as components of the structure of the antibiotic gramicidin C. The role of the carboanhydride bond, actualized synthetically, still remains obscure, since it likewise found no reflection in the quantitative determination of diketopiperazines and tripeptides in the protein molecule. We hope to develop these aspects in later experiments.

EXPERIMENTAL

Our investigations on the determination of copper numbers were carried out on proteins on which preliminary determinations were made of the number of cyclic forms of bonds. The sturin -sulfate and blood albumin which we used were analyzed by A.V. Koperine. Our sturin sulfate was prepared by N.N. Yarovenko from the milt of Russian sturgeon by the combination method of Kossel [9] and Malenilk [10].

Blood albumin was isolated from human blood, purified by dialysis and precipitated with acetone in the cold. The casein used was commercial Kahlbaum materials (Hamarsten's grade). We prepared gliadin from wheat gluten and purified it by repeated reprecipitation from aqueous ethanol and from a mixture of ethanol and ether. Photographic gelatin was purified by Leb's method; at 110° its water content was found to be 13.5%. Gramicidin C was recrystallized from aqueous ethanol.

Preparation of Copper Biuret Solutions of Proteins

To a weighed amount of about 0.2 g protein were added 10 to 15 ml 2% $CuCl_2$ solution and 25 to 30 ml 2% NaOH solution. After standing for an hour the excess copper hydroxide was removed by centrifuging and definite volumes, containing 0.025-0.030 g protein, i.e. 0.25-0.30% solutions, were taken for spectrophotometric measurements. The spectrophotometric curves were plotted with the help of the SF-4 spectrophotometer.

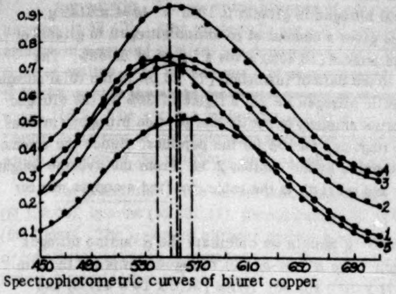
Determination of Copper in Copper Biuret Solutions of Proteins

The copper biuret solution of protein was centrifuged and 15 to 25 ml transparent solution of the copper complex, containing 0.1-0.15 g original protein was taken This solution was ashed with 4 ml conc. sulfuric acid by the Kjeldahl method. After combustion. the contents were transferred into 50 ml water in a flask and titrated iodometrically for copper with 0.5 N thiosulfate solution. In Table 1 are set forth the values of the optical densities of the proteins investigated by us; the diagram shows the spectrophotometric curves of these proteins.

The amount of peptide nitrogen (the nitrogen of the α-amino groups) is calculated by multiplying by 14 the amount of amino acids in the molecule of the given protein (as calculated for example from Tristram's tables [6]) and dividing the resultant number per g nitrogen into 10^5 g protein. From the α-amino nitrogen by deduction of the nitrogen of the cyclic forms of bonds we find the nitrogen of the peptide forms of bonds. By determination of the percentage ratio of peptide nitrogen to cyclic nitrogen we arrive at the relative amounts of cyclic and linear α-amino nitrogen. From these ratios we calculate the proportion of cyclic nitrogen required for the three nitrogens of the tripeptide. To the number of the average amino acid residue in the tripeptide we add the mean amino acid residue in the cyclic forms of bonds calculated on the basis of the ralative amounts in the protein molecule of proline, hydroxyproline, phenylalanine, leucine and (in part) alanine and glycine, which are most frequently met with in rings.

For sturin sulfate. As an example we give the procedure for determining the average molecular weight of the amino acid entering the ring. Of all the amino acids of sturin sulfate, leucine, alanine, and serine participate in the cyclic forms of the bond in the ratio of 1:2:2, i.e. 5 amino acids in all. By multiplying the molecular weights of these amino acids by their number, adding them all and dividing by 5, we obtain the mean residual weight of the amino acid in the peptide. This number is equal to 109.4. and without water to 91.4. 10 molecules of arginine. 2 molecules of histidine and 3 molecules of lysine are linked in the peptides, and these 15 amino acids of basic character are combined with 8 molecules of sulfuric acid. The total molecular weight of these amino acids together with the 8 molecules of sulfuric acid is 3273. Hence the average residual weight of the amino acid participating in the peptide forms of the bond is equal to 3273: 15 = 218, or 200 (without water). In the case of proteins containing moisture, the α-amino nitrogen must be calculated with allowance for the real content of total nitrogen in the protein examined.

The copper number of sturin sulfate is calculated by adding together the average residual weights of the amino acids in the ring and in the tripeptide, i.e. 600 + 91.4 or 691.4.



Spectrophotometric curves of biuret copper complexes of proteins

1) Gelatin max.(565 mμ), 2) edestin (555 mμ), 3) casein max: (552.5 mμ), 4) blood albumin (550 mμ), 5) sturin -sulfate (540 mμ).

TABLE 1

Optical Densities of Copper Biuret Complexes of Various Proteins

Wave length (in mμ)	Concentration of solutions (in %)						
	0.32	0.25	0.36	0.22	0.25	0.25	0.25
	sturin-sulfate	casein	albumin	proto-acid	gliadin	edestin	gelatin
450	0.236	0.133	0.268	0.113	0.136	0.182	0.092
460	0.286	0.166	0.308	0.138	0.158	0.221	0.126
470	0.350	0.211	0.366	0.176	0.201	0.271	0.168
480	0.426	0.268	0.442	0.224	0.247	0.331	0.217
490	0.508	0.332	0.514	0.275	0.298	0.402	0.271
500	0.584	0.403	0.606	0.327	0.361	0.484	0.324
510	0.651	0.467	0.684	0.380	0.419	0.561	0.377
520	0.693	0.528	0.754	0.430	0.470	0.623	0.424
530	0.718	0.572	0.800	0.465	0.509	0.682	0.460
540	**0.731**	0.599	0.822	0.486	0.534	0.708	0.488
545	0.721	0.608	–	0.491	–	0.717	0.496
550	0.718	**0.615**	0.832	**0.493**	0.537	0.719	0.508
555	0.702	**0.615**	0.826	**0.493**	**0.544**	**0.721**	0.511
560	0.671	0.609	0.822	0.489	0.539	0.711	0.513
565	–	–	–	0.488	–	–	**0.513**
570	0.636	0.598	0.792	0.481	0.527	0.701	0.513
580	0.558	0.585	0.764	0.463	0.501	0.675	0.503
590	0.541	0.576	0.714	0.445	0.481	0.638	0.486
600	0.481	0.549	0.662	0.412	0.445	0.589	0.461
610	0.428	0.508	0.604	0.377	0.405	0.527	0.425
620	0.361	0.462	0.546	0.341	0.363	0.483	0.387
630	0.312	0.420	0.474	0.299	0.316	0.407	0.344
640	0.265	0.371	0.412	0.267	0.281	0.367	0.298
650	0.222	0.327	0.354	0.232	0.244	0.316	0.256
660	0.190	0.273	0.304	0.197	0.211	0.267	0.217
670	0.157	0.233	0.256	0.167	0.183	0.226	0.184
680	0.092	0.197	0.218	0.142	0.156	0.187	0.155
690	0.083	0.167	0.190	0.124	0.136	0.158	0.128
700	0.069	0.147	0.162	0.106	0.116	0.133	0.107
710	0.058	0.119	0.138	0.098	0.099	0.113	0.087

For gliadin. Of the 855 amino acids entering into 10^5 g protein, ammonia constitutes 321 molecules, arginine 15.75, histidine 11.75, lysine 4.45, and tryptophane 3.0 molecules. Arginine contains 42 g non-amino nitrogen in the molecule, i.e. in all 15.75 x 42 = 661.5 g; histidine has 11.75 x 28 = 329.0 g non-amino nitrogen; lysine contains 4.45 x 14 = 62.3 g amino nitrogen; tryptophane has 3 x 14 = 42 g. Ammoniacal nitrogen = 321 x 14 = 4494 g. The total of α-non-amino nitrogen and ammoniacal nitrogen in gliadin is 1655 + 4494 = 6149 g, equivalent to 34.8% of the total nitrogen. Our calculation thus gives a content of α-amino nitrogen in gliadin of 65.2%, which recalculated to total nitrogen in the investigated protein (16.40%) gives a figure of 60.53%. The nitrogen in the cyclic forms in gliadin constitutes, according to the data of Ioanisiani [7], 26.5% of the total nitrogen. From the difference between the α-amino nitrogen and the cyclic nitrogen we get a figure of 34% for the nitrogen of the peptide forms of the bonds. We then calculate the relative amounts of cyclic and peptide nitrogen (in relation to the α-amino nitrogen). The values are 43.83% for the rings and 56.15% for the peptides. Hence the amount of cyclic forms of the bonds required for the tripeptide is represented by the number 2.34. From the average weights of the amino acids entering into the ring and the "tripeptide" and set forth in the table, we find a copper number for gliadin of 545.9.

For gelatin. Out of the 1100 amino acids entering into 10^5 g protein we calculate the α-amino nitrogen from the difference between 100 and the α-non-amino nitrogen. The α-non-amino nitrogen comprises the sum of the nitrogens of arginine (49.2 x 42 = 2066.4), histidine (4.71 x 28 = 131.88), lysine (31.5 x 14 = 441.0) and ammonia (5.3 x 14 = 74.2) and is equal to 2713.48 or 15.08% of the total nitrogen. Hence the α-amino nitrogen of gelatin is equal to 84.9%, or recalculated to the total nitrogen of the actual protein (16.24%) the α-amino nitrogen amounts to 76.6%. The cyclic nitrogen of gelatin, according to electroreduction data, is 23.5%. From the difference between the α-amino nitrogen and the cyclic nitrogen we find a value of 53.1% for the nitrogen of the peptide groups. We then calculate the relative amounts of linear and of cyclic nitrogens to α-amino nitrogen, the respective values being 69.33 and 30.68%. Hence the number of rings required for a tripeptide is expressed by the number 1.33.

Of all the amino acids of gelatin the rings contain proline, hydroxyproline, phenylalanine and glycine in the following amounts: proline + hydroxyproline 134.5 moles; phenylalanine 25 moles; glycine 109 moles. The total molecular weight of these acids is 28859, and therefore the average molecular weight of the amino acids associated with the ring is obtained by dividing 28859 by the sum of all the amino acids of the ring (268.5 moles) and is equal to 107 or, with deduction of water, 89. The average molecular weight of the amino acids in the peptides is 73.2. The copper number of gelatin is equal to 383.6 after allowing for the water, which comprises 13.5% of the total weight of gelatin.

For albumin. From the 846 amino acids entering into 10^5 g protein, we calculate the α-amino nitrogen from the difference between the α-non-amino nitrogen and 100. The α-non-amino nitrogen is determined from the sum of the nitrogens of arginine (35.7 x 42 = 1499.4), histidine (22.6 x 28 = 632.8), lysine (84.3 x 14 = 1180.2) and ammonia (63 x 14 = 882) and is equal to 4194.4 or 26.29% in relation to the total nitrogen of albumin. Hence the α-amino nitrogen of albumin is 73.71%. The cyclic nitrogen in albumin is 21.6% of the total nitrogen of the protein; consequently the figure for peptide nitrogen is 52.11%. The relative amounts of linear and cyclic forms of the bonds are expressed by the numbers 70.68 and 29.30, while the number of rings required per tripeptide is represented by the number 1.24.

The copper number of albumin taking into account the average molecular weights of the amino acids in the ring and the peptide set forth in Table 1, is 463.6.

For casein.* The α-amino nitrogen of casein, according to Hamarsten, calculated from the amino acid composition and a total nitrogen content of 15.76%, is equal to 73.79%. Conversion to the total nitrogen of the investigated protein (14.80%) gives a figure of 69.29%. The cyclic nitrogen content of casein (22.9% of the total nitrogen) enables determination of the nitrogen of the peptide groups (46.4%). The relative amounts of linear and cyclic forms of bonds in casein in relation to the α-amino nitrogen are expressed by the numbers 66.95 and 33.05% respectively. Hence the number of rings per tripeptide is calculated from the expression:

$$x = \frac{33.05 \cdot 3}{66.95} = 1.5.$$

The copper number of casein is the sum of the average molecular weights of the 3 amino acids in the peptide and of the 1.5 amino acids in the ring together with the quotas of carbohydrate group and phosphoric acid; it is equal to 565.4.

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*The α-amino nitrogen of proteins, calculated from the amino acid composition and the total nitrogen, agrees with that calculated on the basis of amino acids containing also nitrogen in other forms than that of α-amino nitrogen.

For edestin. The α-amino nitrogen of edestin, taking into account its amino acid composition and total nitrogen, is 58.43%. Ring nitrogen in edestin is represented by 18.1% and peptide nitrogen by 40.33%. The relative amounts of rings and peptides are determined from the ratios of their absolute amounts of amino acids: 1 molecule of proline, 3 of leucine and 1 of phenylalanine. The total of the molecular weights of all these amino acids is 673.53, so that the mean molecular weight of the amino acid associated with the ring is 134.7 or (allowing for water) 116.7. The average molecular weight of the amino acid in the peptides is 99.4. The copper number of edestin is the sum of the molecular weights of the amino acids in the ring and tripeptide, allowing for the non-amino nitrogen of the prosthetic groups, and is equal to 486.

For gramicidin. The amino acid composition of gramicidin hydrochloride is: valine (M 117.1), proline (M 115.08), leucine (M 131.11), phenylalanine (M 165.09), and ornithine (M 132.13) in amounts of 2 moles (for dimer). The α-amino nitrogen derives from 10 amino acids present in the gramicidin molecule, while the α-non-amino nitrogen is represented by the two nitrogens of ornithine. In Table 2 we set forth the results of copper determination and of theoretical calculations of the copper numbers. In column 4 the nitrogen of the α-amino groups is calculated in relation to the total nitrogen in the same protein which we analyzed.

For sturin -sulfate, blood albumin, edestin and gramicidin, the nitrogen of the α-amino acids corresponds to the anhydrous preparations. In column 6 the amount of cyclic nitrogen is given as a percentage of the total nitrogen of the α-amino groups, which also represent the main skeleton of the monomer or polymer of the protein, characterizing its participation in the total structure of the protein molecule. Columns 6 and 8 show the relative numbers of cyclic and linear bonds in the protein molecule; in all cases the linear bonds predominate over the cyclic. This relation is quantitatively expressed in column 9. Only gelatin gave copper numbers higher than the theoretical. An attempt to explain this phenomenon, by analogy with gramicidin, by formation of a complex in course of time was not justified. The copper number of gelatin determined 30 minutes after the instant of formation of the copper complex was 489.0. The copper number 48 hours after the start of the reaction was 487.

EVALUATION OF RESULTS

On analyzing the results of the investigations summarized in Table 2 both from the aspect of the number of linear forms of bonds and from that of the content of cyclic structures, we can recognize the important role of the latter in the structure of protein. Thus, in sturin - sulfate one quarter of the α-amino bonds (24%) are cyclic and 44% of these bonds are in gliadin. Consequently the diketopiperazine theory advanced by N.D. Zelinsky and V.S. Sadikov, expressing the important role of cyclic anhydrides, has found further confirmation in a quantitative study of protein structure. In proteins on the average about 33% of the α-amino nitrogen is present in derivatives of piperazines.

The uncertainty about the tripeptide structure with a linear-anhydride character (peptide) has also been fully cleared up in our research. Thus in proteins about 70% of the α-amino nitrogen is present in linear forms of the amino acids system.

The N-aminoacyl form of linkage, experimentally demonstrated by us in the structure of gramicidin C, is still the object of research and evaluation in the case of proteins. In this connection attention may be drawn to the role of the amidine linkage which stabilizes the piperazine-tripeptide structure in the protein monomer. This circumstance must be taken into consideration when separating protein from its system. This form of linkage leads us on the basis of the data of the present investigation to suggest a possible participation of the linkage in question both in the formation of monoamidino-piperazinic structures and in the formation of structure (II). This conclusion is suggested by an analysis of the number of amino acids present in rings and peptides (Table 5).

From these considerations it follows that for each tripeptide in gramicidin there is present 1 piperazine, and that 1 piperazine in sturin is linked to 2 tripeptides. In the remaining proteins we have extremely complex associations of tripeptides with rings, to a considerable extent approximating to system (II) see section below on structure of gramicidin).

Structure of Gramicidin

As we know, apart from "violet" copper complexes, proteins also form "red" complexes (Table 3). Unfortunately these "red" complexes have not yet been adequately investigated with reference to the characterization of their fourth nitrogen.

We suggest that the fourth nitrogen atom may be:

1) The nitrogen of amides of tripeptides containing dicarboxylic acids.

TABLE 2

Protein	Number of acids	Total nitrogen (%)	Nitrogen of α-amino groups to total nitrogen (%)	Nitrogen of cyclic forms of bonds (%)		Nitrogen of peptide forms of bonds (%)		Number of amino acids in ring/3 amino acids in peptide	Average weight of amino acids		Weight of prosthetic groups (carbohydrates, phosphorus, sulfur)	Grams protein combining with 1 g-atom copper	
				total nitrogen *	α-amino group nitrogen	total nitrogen	amino group nitrogen		in peptide	in ring		calculated	found
Surin-sulfate	579	23.37	35.10	8.4	23.93	23.70	78.63	1	200	91.4		691.4	691; 683
Blood albumin	846	15.95	73.71	21.6	29.30	52.11	70.68	1.24	100.2	131.1	0.5 carbohydrate	463.6	453; 462
Casein, Hamarsten's data (15.76)	831	14.80	69.29	22.9	33.05	46.4	66.95	1.5	119.1	120	25 phosphorus, carbohydrates 3.1	565.4	568; 569
Gliadin (17.66)	855	16.40	60.53	26.5	43.83	34.0	56.15	2.34	98.2	107.4		545.9	559; 576
Edestin	827	18.55	58.43	18.1	30.94	40.33	69.05	1.34	99.4	116.7	1.7% or 31.1 non-amino nitrogen (on total)	486	486; 489
Gelatin (18.0)	1100	16.24	76.6	23.5	30.68	53.1	69.33	1.33	73.2	89	13.5% water	383.6	489; 487
Bramicidin	10	13.25	33.4	33.2	40.0	50.2	60.19	2	108.8	122.1	36.5% hydrochloric acid and 36 water	643	646

• As determined by the method of Koperina and Ioanisian.

It has been shown [5] that a tripeptide containing asparagine shifts the maximum of absorption in the direction of short waves. It is not excluded that proteins, which contain considerable amounts of asparagine, utilize the amido nitrogen of this amino acid in the formation of the copper complex, for example in the case of gliadin.

2) Derived from acylamino structures in which the nitrogen of piperazine starts to function as amide nitrogen (piperazide), as in the structure of gramicidin C.

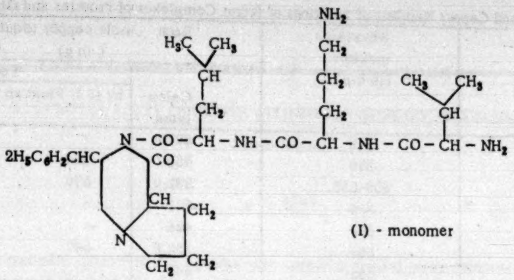
3) The nitrogen of penta- and hexapeptides present in the protein molecule.

4) Finally, as shown by Plekhan, functional groups of amino acids: the amidine nitrogen of histidine and the β-hydroxy group of threonine [5] can shift the absorption maxima in the direction of short waves.

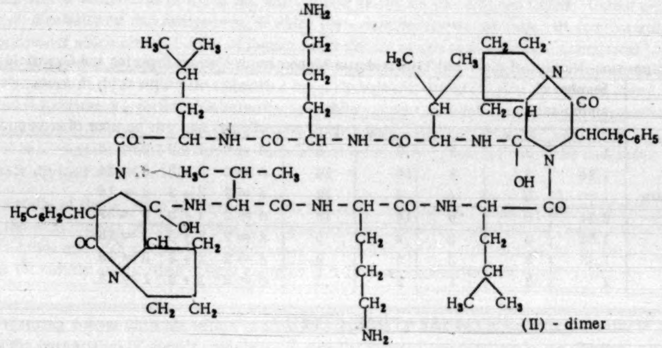
Up to now we have no conclusive proof of participation of the fourth nitrogen in the copper complex according to one of the above-submitted structures. Only investigations on models containing the above-submitted structures in conjunction with piperazine structures and with participation of known forms of linkages (peptide, cyclic, amidine and acylpiperazine) and comparison with proteins will give the key to solution of this interesting problem.

Concerning the copper numbers of protein (Table 4), these actually express the numbers of both linear and cyclic groupings in the protein molecule.

Consequently from the ratios of amino acids bound in cyclic and linear anhydrides and with utilization of the formula of one of the authors (N.I. Gavrilov) we can derive the amino acid composition of the monomers of individual proteins (Table 5).



(I) - monomer



(II) - dimer

TABLE 3

Maxima of Absorption of Solutions of Copper Biuret Complexes of Proteins and the Amount of "Violet" and "Red" Complexes Present in them, Calculated from an Artificial Mixture of Peptides

Protein	Absorption maximum (in mμ)	Percentage of "red" complex calculated from a mixture of		Percentage of "violet" complex calculated from a mixture of	
		penta- and tripeptide	tetra- and tripeptide*	penta- and tripeptide	tetra- and tri-peptide*
		515/570	525/570	515/570	525/570
Sturin sulfate	540	54	30	46	70
Blood albumin	550	39	13	61	87
Hamersten's casein	550-555	31	10	69	90
Gliadin	555	30	7	70	93
Edestin	555	30	7	70	93
Gelatin	565	15	2	85	98
Gramicidin	535	38	62	62	38

SUMMARY

1. A number of proteins were characterized on the basis of their copper numbers and determination were made of the cyclic forms of linkages in their structure and of the absorption spectra of the copper complexes.

2. The determined copper numbers of the proteins quantitatively reflect the participation in the structure of protein of linear and cyclic forms of bonds.

3. Analysis of the absorption curves leaves open the question of the sources of the complexes formed by copper with four atoms of nitrogen.

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*From M.I. Plekhan's curve

TABLE 4

Absorption Maxima and Copper Numbers of Solutions of Biuret Complexes of Proteins and Gramicidin

Protein	Absorption maxima (in mμ)	Each mole copper requires protein (in g)		
		Calculated	Found: by M.I. Plekhan	Found: by us
Sturin sulfate	540	691.4	-	691;683
Blood albumin	550	463.6	394	453;462
Hamersten's casein	550-555	532.0	570	568;569
Gliadin	555	520	-	559;576
Edestin	555	486	-	486;489
Gelatin	565	383.6	547	489;487
Gramicidin	535	643	-	646

TABLE 5

Amino Acid Composition, Number of Rings and Tripeptides in Monomers of Various Proteins and Gramicidin

Protein	Number of amino acids in:		Multiplier	Number of amino acids in:		Number of amino acids in monomer from formula $A = 2x + 3y$, where x is number of rings and y is number of tripeptides
	ring	peptide		ring	peptide	
Sturin sulfate	1	3	2	2	6	$A = 2 \cdot 1 + 3 \cdot 2 = 8$
Blood albumin	1.24	3	8	10	24	$A = 2 \cdot 5 + 3 \cdot 8 = 34$
Hamersten's casein	1.5	3	4	6	12	$A = 2 \cdot 3 + 3 \cdot 4 = 18$
Gliadin	2.34	3	6	14	18	$A = 2 \cdot 7 + 3 \cdot 6 = 32$
Edestin	1.34	3	3	4	9	$A = 2 \cdot 2 + 3 \cdot 3 = 13$
Gelatin	1.33	3	3	4	9	$A = 2 \cdot 2 + 3 \cdot 3 = 13$
Gramicidin	2	3	1	2	3	$A = 2 \cdot 1 + 3 \cdot 1 = 5$

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** See Consultants Bureau Translation, p. 2077, 2085.

*** " " " " p. 341, 347, 635.

**** " " " " p. 1675.

***** " " " " p. 371.

INNER COMPLEX SALTS OF AZO COMPOUNDS

I. COMPLEX SALTS OF COPPER WITH SOME o-MONOHYDROXYAZO COMPOUNDS

V. I. Mur

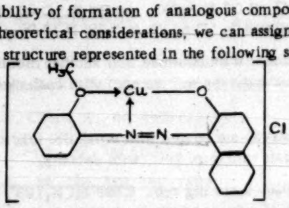
Among the inner complex salts of azo compounds with copper, a special group comprises the complexes of o-monosubstituted compounds in which the salt-forming groups are OH, NH_2 and COOH. Unlike copper complex salts of o,o'-disubstituted azo compounds, in which the o-substituents are the same salt-forming groups and into the composition of which enters 1 atom of copper per molecule of azo compound (1:1 complexes) [1,2], copper salts of non-sulfonated o-monosubstituted azo compounds contain 1 atom of metal per two molecules of azo compound (1:2 complexes) [1-10]. Non-sulfonated copper complexes of the simplest o,o'-disubstituted azo compounds of the above-mentioned type were prepared by interaction of ethanolic solutions of the corresponding azo compounds with copper chloride [2], and complexes of o-monosubstituted compounds by interaction of an ethanolic solution of azo compound with an aqueous ammoniacal solution of copper sulfate, or by interaction with the metal in the finely divided state [2-10].

In a study of the relation between structure and some properties of copper complexes of azo compounds, we repeated the experiments of the previous investigators [2] and obtained complexes of copper with o-hydroxybenzeneazo-β-naphthol and with o-carboxybenzeneazo-β-naphthol of the 1:1 composition; in the same conditions we obtained the previously undescribed copper complex of o-carboxymethoxybenzeneazo-β-naphthol* of the 1:1 composition.

By reacting copper chloride with o-methoxybenzeneazo-β-naphthol in conditions similar to those indicated above for the preparation of copper complexes of o,o'-disubstituted azo compounds, we obtained a new complex of 1:1 composition differing both in composition and properties from the complex obtained by the previous investigators [2,6,8] from the same azo compound. We obtained a similar complex (1:1 composition) also from 1-phenyl-3-methyl-4-(o-methoxybenzeneazo)-5-pyrazolone. Treatment of the prepared complexes with aqueous ammonia converts them into 1:2 complexes identical with those obtained in the working conditions of Crippa [6]; the interaction is accompanied by loss of one atom of copper and two atoms of chlorine per 2 molecules of initial complex. Mineral acids decompose these complexes with separation of the original dyes.

Azo compounds from o-chloroaniline and o-nitroaniline, as diazo components, and β-naphthol and 1-phenyl-3-methyl-5-pyrazolone, as azo components, do not form 1:1 complexes with copper. Their complexes with copper of the 1:2 composition are formed smoothly.

On the basis of the properties of the prepared copper salts of o-hydroxy-o'-methoxyazo compounds with 1:1 composition (absence of ionized copper, positive though weak reaction for chlorine ion, their transformation into 1:2 complexes, formation of the original azo compounds by the action of mineral acids), of the data of elementary analysis, of the impossibility of formation of analogous compounds from o-chloro- and o-nitro-o'-hydroxyazo compounds and of general theoretical considerations, we can assign to the compound of o-methoxybenzeneazo-β-naphthol with copper the structure represented in the following scheme:



An analogous structure may be assigned to the copper compound of 1-phenyl-3-methyl-4-(o-methoxybenzeneazo)-5-pyrazolone.

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* Although it is known [11] that the group of o-carboxymethoxy-o'-hydroxyazo compounds is susceptible to complex formation, the corresponding complexes have not been prepared in the pure state or analyzed.

EXPERIMENTAL

The starting monoazo compounds were prepared by the usual route, recrystallized from glacial acetic acid, washed with ethanol and identified from the melting points.

The C, H and N contents of the complexes were determined by elementary microanalysis; for determination of the content of Cu, Cl and azo compound in the complexes, the latter were decomposed with sulfuric acid, the dye was filtered off on a Schott funnel, and the copper in the filtrate was determined iodometrically and the chlorine by Mohr's method.

Copper salt of o-carboxymethoxybenzeneazo-β-naphthol. The azo compound from o-amino-phenoxyacetic acid (prepared by Thate's method [12] in the form of the potassium salt) and β-naphthol was obtained by coupling the components in an alkaline medium in very dilute solutions. Red needles soluble in organic solvents, sparingly soluble in water, m.p. 242°.

6.362 mg sub.: 15.536 mg CO_2; 2.346 mg H_2O. 3.204 mg sub.: 0.242 ml N_2 (22.5°, 738.2 mm). Found%: C 66.64; H 4.12; N 8.47. $C_{18}H_{14}O_4N_2$. Calculated %: C 67.08; H 4.35; N 8.69.

To a hot ethanolic solution of the azo compound was added an ethanolic solution of copper chloride, and the mixture was left to crystallize. The separated copper salt was washed with hot ethanol. Brown needles not melting up to 360°.

4.588 mg sub.: 9.480 mg CO_2; 1.272 mg H_2O. 3.056 mg sub.: 0.210 ml N_2 (22.4°, 737.8 mm). 0.2567 g sub.: 6.63 ml 0.1 N $Na_2S_2O_3$. Found %: C 56.43; H 3.11; N 7.71; Cu 16.42. $C_{18}H_{12}O_4N_2Cu$. Calculated %: C 56.31; H 3.13; N 7.30; Cu 16.57.

Copper salt of methoxybenzeneazo-β-naphthol (1:1). Prepared in the conditions of the preceding experiment. Fine, brown needles not melting when heated to 360°.

6.338 mg sub.: 12.607 mg CO_2; 2.090 mg H_2O. 3.705 mg sub.: 0.288 ml N_2 (24°, 726 mm). 0.3830 g sub.: 10.09 ml 0.1 N $Na_2S_2O_3$. 0.5162 g sub.: 13.91 ml 0.1 N $AgNO_3$. Found%: C 54.28; H 3.69; N 8.53; Cu 16.75; Cl 9.57. $C_{17}H_{13}O_2N_2ClCu$. Calculated %: C 54.24; H 3.46; N 8.22; Cu 16.90; Cl 9.44.

It was decomposed by sulfuric acid to form the original dye with m.p. 177.5-178° (no depression of melting point in mixed test).

On shaking with an alcoholic solution of ammonia it is transformed into a crystalline substance with m.p. 221.5-222°, not giving a melting point depression with the substance obtained in Crippa's [6] working conditions and having a 1:2 composition.

0.3186 g sub : 5.19 ml 0.1 N $Na_2S_2O_3$; 0.2857 g azo compound. Found%: Cu 10.33; azo compound 89.67. $(C_{17}H_{13}O_2N_2)_2Cu$. Calculated %: Cu 10.29; azo compound 90.02.

Interaction is accompanied by separation of copper and chlorine, as indicated by the blue coloration of the solution characteristic of cuprammonium and by a definite reaction for chlorine with $AgNO_3$.

Copper salt of 1-phenyl-3-methyl-4-(o-methoxybenzeneazo)-5-pyrazolone (1:1). Prepared in the conditions of the preceding experiments but in a methanolic medium. Greenish-yellow hair-like needles, not melting up to 360°.

5.708 mg sub.: 10.592 mg CO_2; 1.832 mg H_2O. 2.800 mg sub.: 0.358 ml N_2 (29°, 729.5 mm). 0.2944 g sub.: 7.24 ml 0.1 N Na_2SO_3. 0.5778 g sub.: 14.47 ml 0.1 N $AgNO_3$. Found %: C 50.[illegible]; H 3.59; N 13.85; Cu 15.63; Cl 8.89. $C_{17}H_{15}O_2N_4ClCu$. Calculated %: C 50.23; H 3.69; N 13.78; Cu 15.65; Cl 8.74.

On heating with an aqueous ethanolic solution it is transformed into another modification – a dark, microcrystalline precipitate (fine greenish-yellow prisms under the microscope) with unchanged composition as confirmed by elementary analysis.

When both of these compounds (1:1 composition) are heated with ethanolic solution of ammonia they are transformed into the 1:2 complex. Brownish crystals with m.p. 285° (with decomp).

6.210 mg sub.: 13.784 mg CO_2; 2.396 mg H_2O. 3.414 mg sub.: 0.528 ml N_2 (29°, 718.2 mm). 0.4958 g sub.: 7.28 ml 0.1 N $Na_2S_2O_3$. Found %: C 60.57; H 4.32; N 16.48; Cu 9.35. $(C_{17}H_{15}O_2N_4)_2Cu$. Calculated %: C 60.21; H 4.43; N 16.53; Cu 9.38.

On interaction of the azo compounds from o-chloroaniline and o-nitroaniline and β-naphthol and 1-phenyl-3-methyl-5-pyrazolone with copper chloride in the conditions of the preceding experiments for preparation of 1:1 complexes, complex formation was not observed; on boiling ethanolic solutions of the above azo compounds with copper chloride and aqueous ammonia solution, the corresponding 1:2 complexes were obtained.

Copper salt of o-chlorobenzeneazo-β-naphthol. Dark, coalescent platelets (under the microscope) with a greenish tinge, m.p. 232° (decomp.).

0.3154 g sub.: 4.94 ml 0.1 N $Na_2S_2O_3$; 0.2840 g azo compound. Found %: Cu 9.96; azo compound 90.04. $(C_{16}H_{10}ON_2Cl)_2Cu$. Calculated %: Cu 10.15; azo compound 90.17.

Copper salt of o-nitrobenzeneazo-β-naphthol. Reddish-brown rods (under the microscope) with a greenish tinge, m.p. 264 (decomp.).

0.2010 g sub.: 3.12 ml 0.1 N $Na_2S_2O_3$; 0.1815 g azo compound. Found %: Cu 9.85; azo compound 90.28. $(C_{16}H_{10}O_3N_3)_2Cu$. Calculated %: Cu 9.82; azo compound 90.43.

Copper salt of 1-phenyl-3-methyl-4-(chlorobenzeneazo)-5-pyrazolone. Lustrous brown plates, m.p. 263° (decomp.).

0.2852 g sub.: 4.24 ml 0.1 N $Na_2S_2O_3$; 0.2588 g azo compound. Found %: Cu 9.45; azo compound 90.74. $(C_{16}H_{12}ON_4Cl)_2Cu$. Calculated %: Cu 9.26; azo compound 91.03.

Copper salt of 1-phenyl-3-methyl-4-(o-nitrobenzeneazo)-5-pyrazolone. Dark-brown prisms, partly coalescent, m.p. 248° (decomp.).

0.2822 g sub.: 4.00 ml 0.1 N $Na_2S_2O_3$; 0.2578 g azo compound. Found %: Cu 8.77; azo compound 91.36. $(C_{16}H_{12}O_3N_5)_2Cu$. Calculated %: Cu 8.98; azo compound 91.29.

All the prepared complexes are quickly decomposed by conc. sulfuric acid to form the original components, and they possess varying stabilities to the action of dilute acids; they are insoluble or poorly soluble in water, soluble in organic solvents, especially readily in chloroform and carbon bisulfide.

SUMMARY

1. Preparation and identification were carried out of new complexes of copper with azo compounds from o-aminophenoxyacetic acid, o-methoxyaniline, o-chloroaniline, and o-nitroanilines as diazo components, and β-naphthol and 1-phenyl-3-methyl-5-pyrazolone as azo components.

2. A possible structure is proposed for the copper complex of o-methoxybenzeneazo-β-naphthol and 1-phenyl-3-methyl-4-(o-methoxybenzeneazo)-5-pyrazolone with 1:1 composition.

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copper chloride and aqueous ammonia solution, the corresponding 1:2 complexes were obtained.

Copper salt of o-chlorophenylazo-β-naphthol. [illegible] m.p. 282° (decomp.).

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

All the copper complexes are [illegible] by conc. sulfuric acid [illegible] the original azo compound [illegible]

SUMMARY

1. [illegible]

2. [illegible]

LITERATURE CITED

[1] [illegible]

[2] [illegible]

[3] [illegible]

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CONCERNING β-NITROVINYL-5-SUBSTITUTED FURANS

Z.N. Nazarova

The versatile properties of 2-furaldehyde permit its extensive utilization for a variety of syntheses and the preparation of a series of interesting and useful products [1].

It is know that substituents like chlorine, bromine and the nitro group increase the stability of the furan nucleus and intensify its bacteriostatic properties. In this connection great interest attaches to the as yet little studied 5-substituted 2-furaldehydes on whose basis can be obtained pharmacologically active substances [2] and insecticides [3].

The possibility of obtaining 5-substituted 2-furaldehydes (chloro-, bromo- and nitro- derivatives) was demonstrated by Gilman[3a]; however, the yield of the respective products was small. A new method for nitration of 2-furaldehyde was recently developed [4] which enabled the preparation from 5-nitro-2-furaldehyde of a series of nitrofuran derivatives possessing valuable bacteriostatic properties. We have shown [5] the possibility of preparation of 5-bromo-2-furaldehyde by direct bromination of 2-furaldehyde in dichloroethane in presence of traces of sulfur and hydroquinone in a yield of 60% of the theoretical.

Very little study has been devoted to condensations with bromo-2-furaldehyde; a series of syntheses described in the literature [6] nevertheless show that the presence of bromine in the furan nucleus does not in the majority of cases hinder the reactivity of the carbonyl group although it increases the stability of the furan ring. All condensations with bromo-2-furaldehyde proceed readily and with good yields of products.

Condensations of 5-bromo- and 5-nitro-2-furaldehyde with nitroparaffins have not previously been described in the literature. We carried out the condensation of 5-bromo-and 5-nitro-2-furaldehyde with nitromethane and chloronitromethane in the conditions described for condensation of 2-furaldehyde with chloronitromethane [7] and obtained: 5-bromofurylnitroethylene (92%); 5-bromofurylchloronitroethylene (83%); 5-nitrofurylnitroethylene (50%); and 5-nitrofurylchloronitroethylene (41%). It should be mentioned that the condensations with bromo-2-furaldehyde proceed with considerably greater facility than with nitro-2-furaldehyde.

5-Bromofurylnitroethylene (see the scheme: I, A = H), obtained by us for the first time, forms lustrous yellow leaflets with m.p. 117-118° (from ethanol), easily soluble in organic solvents; it distils with steam and possesses an irritant action.

Although furylnitroethylene has been known for a long time [8], its bromination has not previously been studied. We brominated furylnitroethylene both in glacial acetic acid and in CCl_4 with heating and obtained a product with m.p. 117-118°, identical with the 5-bromofurylnitroethylene obtained as described above.

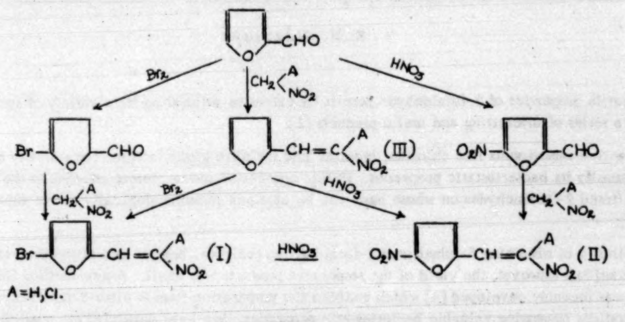
The 5-nitrofurylnitroethylene (II, A = H), obtained by us by direct synthesis, was identical with the product of nitration of furylnitroethylene previously described by Priebs [8] and forms yellow needles (from ethanol) with m.p. 142-143°.

In the course of study of the properties of the product of condensation of chloronitromethane with 2-furaldehyde, Tsukervanik and Potemkin [7] studied the bromination and nitration of furylchloronitroethylene (III, A = Cl) and obtained respectively a bromination product with m.p. 74-75° and a nitration product with m.p. 83-84°. On the basis of literature data and of the transformation of the bromo- into the nitro- derivative under the action of nitric acid (d 1.2) the authors assumed that the most probable structures were 5-bromo- and 5-nitro-substituted β-nitrovinylfurans. A direct comparison by us showed that these products were actually 5-bromofurylchloronitroethylene and 5-nitrofurylchloronitroethylene, which we prepared by condensation of 5-bromo- and 5-nitro-2-furaldehydes with chloronitromethane.

It is interesting to note the interchangeability of the 5-bromo derivatives with the corresponding 5-nitro derivatives: on heating 5-bromofurylnitroethylene and 5-bromofurylchloronitroethylene with nitric acid, 5-nitrofurylnitroethylene and 5-nitrofurylchloronitroethylene, respectively, are formed; the bromine atom in the 5-position is replaced by a nitro group with liberation of free bromine. Similar exchange reactions of halogen in the furan nucleus have been described in the literature [7]. In these conditions bromo-2-furaldehyde does not give nitro-2-furaldehyde.

The fact has thus been verified that bromination of β-nitrovinylfurans is not accompanied by addition of bromine at the double bond of the side chain, but that in the first instance the α-hydrogen in the furan nucleus is substituted; nitration likewise yields 5-nitro-substituted β-nitrovinylfurans.

All the transformations described above are summarized in the scheme.



EXPERIMENTAL

5-Bromo-2-furaldehyde [5]. To a solution of 28.8 g (0.3 mole) 2-furaldehyde * in 120 ml dichloroethane was added 0.005 g each of sulfur and hydroquinone and with heating on a water bath (reflux condenser with a lead-off tube at the end) addition was made from a dropping funnel of a solution of 57.5 g (0.32 g-mole) bromine in 150 ml dichloroethane at such a speed that the Br entered into reaction. After all the bromine had been added (3 hours), heating was contined until hydrogen bromide ceased to be evolved (about 3 hours). The reaction mixture was then steam distilled. After the solvent had been driven off, yellowish crystals of bromo-2-furaldehyde appeared in the condenser. The bromo-2-furaldehyde was collected, washed with cold water and dried. Yield 32 g (60.7%). The crude product had m.p. 79-80°. Recrystallization from 50% ethanol gave colorless needles with m.p. 82°.

5-Nitro-2-furaldehyde was obtained by nitration of 2-furaldehyde with nitric acid (d 1.52) in presence of acetic anhydride, followed by saponification of the nitro-2-furaldehyde diacetate with sulfuric acid [9].

Chloronitromethane was prepared by Chernyak's method [10] of chlorination of the sodium salt of nitromethane.

I. 5-Bromofurylnitroethylene

Prepared by two methods. a) Condensation of nitromethane with bromo-2-furaldehyde. To a well-cooled (ice and salt) solution of 3.5 g (0.02 mole) bromo-2-furaldehyde and 1.62 g (0.026 mole) nitromethane in 15 ml methanol was added, dropwise with shaking, a solution of 0.8 g (0.02 mole) NaOH in 5 ml water. The conclusion of addition of the alkali was followed by separation of a voluminous precipitate of the sodium salt of bromofurylnitroethanol. The mixture was left for 20 minutes in a freezing mixture, after which water with ice was added to dissolve the precipitate (about 20 ml). With vigorous stirring the well-cooled mixture was run dropwise into 7 ml 10% hydrochloric acid (cooled to -5°) at such a rate that the temperature did not rise above 0°. The precipitate was separated, washed with cold water and distilled with steam. Yield of yellow crystals with m.p. 116-118° 4 g (92%); recrystallization from ethanol gave yellow platelets with m.p. 117-118°, readily soluble in organic solvents, insoluble in water.

0.0988 g sub.: 0.0855 g AgBr. Found %: Br 36.82. $C_6H_4O_3NBr$. Calculated %: Br 36.70.

b) Bromination of furylnitroethylene.** Furylnitroethylene, prepared in a similar manner by condensation of 2-furaldehyde with nitromethane in a yield of 77% (m.p. 74-75°), was brominated in the conditions described for bromination of ethyl-α-cyano-β-furylacrylate [6b]. To a solution of 2 g (0.014 mole) furylnitroethylene in 7.5 ml hot glacial acetic acid was added dropwise a solution of 2.5 g (0.014 mole) bromine in 3 ml glacial acetic acid. The mixture was refluxed until cessation of evolution of HBr (about 1 hour); after cooling, the solution was diluted with water and the resultant precipitate was separated, washed with water and steam distilled. The crystals which came over were twice recrystallized from ethanol – yellow leaflets with m.p. 117-118°. No melting point depression [illegible] in admixture with 5-bromo-furylnitroethylene. The same product with m.p. 117-118° was isolated after bromination of furylnitroethylene in CCl_4.

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* Technical 2-furaldehyde was purified by washing with Na_2CO_3 solution (10%) and cold water, drying with Na_2SO_4 and distilling in a column (12 theoretical plates), b.p. 159° (727 mm). The bromine and dichloroethane were dried over calcined $CaCl_2$.

** With participation of Bugrova.

II. 5-Nitrofurylnitroethylene

Obtained by three methods. a) Condensation of nitro-2-furaldehyde with nitromethane was carried out in a similar manner to the condensation of bromo-2-furaldehyde. Components were 2.8 g (0.02 mole) nitro-2-furaldehyde, 1.22 g (0.02 mole) nitromethane, 5 ml methanol, 1 g NaOH in 5 ml water and 7 ml 10% hydrochloric acid. A precipitate did not appear when caustic alkali solution was added and no crystals separated when poured into cooled hydrochloric acid, but an oil formed which solidified only after dilution with water and prolonged shaking. After two recrystallizations from ethanol, orange-yellow crystals were obtained with m.p. 142-143°.

Nitrofurylnitroethylene is not volatile in steam; it is soluble in organic solvents; with caustic alkalies it gives a deep-colored solution which rapidly darkens.

b) Interaction of bromofurylnitroethylene with nitric acid. A mixture of 2.18 g (0.01 mole) bromofurylnitroethylene and 7 ml nitric acid (d 1.2) was heated until an exothermic action commenced to the accompaniment of evolution of free bromine. The bromonitrofurylethylene completely dissolved. The mixture was diluted with water, neutralized with $NaHCO_3$ solution and extracted with ether. From the ethereal solution isolated yellow crystals which after two recrystallizations from ethanol melted at 142-143° and did not contain halogen. A mixed test with 5-nitrofurylnitroethylene did not give a depression of melting point.

c) Nitration of furylnitroethylene. To 8.35 g (0.13 mole) nitric acid (d 1.52) with cooling (not above -5°) was gradually added (in the course of 0.5 hour with mechanical stirring) 2 g (0.014 mole) furylnitroethylene. After all had been added (the mixture solidified) addition was made of 5 ml glacial acetic acid and the stirring was continued for another 2 hours at 0°. The whole mass was then poured into 70 ml crushed ice; 15 minutes later the precipitate was separated, washed with water and dried between sheets of filter paper. Yield of crude product 2.6 g (98%), m.p. 132-134°. Recrystallization from ethanol gave 1.6 g (60.54%) yellow-orange crystals with m.p. 142-143°. A mixed test with 5-nitrofurylnitroethylene did not give a depression of m.p.

III. 5-Bromofurylchloronitroethylene

Condensation of bromo-2-furaldehyde with chloronitromethane. Components were 3.5 g (0.02 mole) bromo-2-furaldehyde, 1.9 g (0.02 mole) chloronitromethane, 15 ml methanol, 0.8 g (0.02 mole) NaOH in 5 ml water and 7 ml 10% hydrochloric acid. Condensation was effected as in the preceding experiments. After pouring into the hydrochloric acid, the reaction mixture was steam distilled to give yellow crystals with m.p. 65-68°. Recrystallization from ethanol gave bright-yellow, lustrous (mother-of-pearl) leaflets with m.p. 74.75°. Yield 4.2 g (83%). A mixed test with the product of bromination of furylchloronitroethylene [7] did not give a depression of melting point.

IV. 5-Nitrofurylchloronitroethylene

a) Condensation of 5-nitro-2-furaldehyde with chloronitromethane. Materials used were 2.3 g (0.02 mole) nitro-2-furaldehyde, 1.9 g (0.02 mole) chloronitromethane, 10 ml methanol, 1 g NaOH in 5 ml water and 7 ml 10% hydrochloric acid. Addition of the alkali brought down a small precipitate and a heavy oil which solidified after dilution with water and prolonged shaking in a freezing mixture. Extraction with ether gave 1.5 g (41.4%) crystalline mass. Two recrystallizations from ethanol gave orange-yellow crystals with m.p. 83-84°. A mixed test with the product of nitration of furylchloronitroethylene [7] did not give a depression of melting point.

b) Reaction of 5-bromofurylchloronitroethylene with nitric acid (d 1.2) yielded crystals with m.p. 83-84°. A mixed test with 5-nitrofurylchloronitroethylene did not give a depression of melting point.

SUMMARY

1. For the first time the condensation was effected of 5-bromo- and 5-nitro-2-furaldehydes with nitromethane and chloronitromethane to give respectively 5-bromofurylnitroethylene (not described in the literature), 5-bromofurylchloronitroethylene, 5-nitrofurylnitroethylene, and 5-nitrofurylchloronitroethylene.

2. It was demonstrated that in the bromination and nitration of furylnitroethylene and furylchloronitroethylene the α-hydrogen of the furan ring is substituted with formation of the 5-bromo and the 5-nitro derivative respectively.

3. It is shown that treatment of 5-bromo-(β-nitrovinyl)-furans with nitric acid converts them into the corresponding 5-nitro derivatives with release of free bromine. In these conditons bromo-2-furaldehyde does not give nitro-2-furaldehyde.

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IN MEMORY OF EVGENY ALEKSEEVICH IVANOV

On January 27, 1953, after a long and serious illness passed away Evgeny Alekseevich Ivanov, head of the central laboratory of the Dorogomilovsk M.V. Frunze Chemical Works, member of the Scientific Council of the K.E. Voroshilov Research Institute for Intermediates and Dyes, Stalin Laureat, one of the leading workers of the aniline dye industry.

E.A. Ivanov was born in 1903 at Saratov in the family of a state teacher. After leaving the intermediate school he went to the Moscow G.V. Plekhanov Institute of National Economy which he left in 1929 with the diploma of engineering technologist. From that time his working life was spent at the Dorogomilovsk Works where he progressed from shift manager to research manager and then to control of the central laboratory. Here E.A. Ivanov completed more than 50 original investigations. These were not remote from practical matters and many of them served as a basis for the organization at the Dorogomilovsk Works of a series of manufactures of intermediates and dyes introduced for the first time to our industry.

Among a number of researches on the larger scale carried out by E.A. Ivanov or under his direction and later adopted by the works, mention should be made of the development of procedures for the manufacture of: p-nitro-o-anisidine, p-toluenesulfochloride, the nitrotoluidines, p-toluidine disulfonic acid, quinizarin, and a series of acid anthraquinone dyes.

We must also put on record the great and carefully executed investigation by E.A. Ivanov of the mechanism and kinetics of formation of dialkylamines from nitrosodialkylanilines.

Under the direction of E.A. Ivanov important studies were initiated by the Dorogomilovsk works collective on the new technology of production of diphenylguanidine and a series of other products. In later years E.A. Ivanov with a large collective undertook important studies which foresaw a change in the technology of production of a series of large-scale intermediates of the aniline dye industry, with the aim of improving the hygienic conditions of operation. For his part in this project, whose results were adopted by the industry, he was granted the title of Stalin Laureate in 1951.

The economic effect of the results of E.A. Ivanov's researches can be reckoned in millions of rubles.

Since 1949 E.A. Ivanov was a member of the Communist Party of the Soviet Union. For his services he was honored with the Order of Worker of the Red Banner, with medals "For Working Valor", , "For Valiant Work in the Great Patriotic War," and "In Memory of 8 Centuries of Moscow".

E.A. Ivanov was a sensitive and sympathetic man and won the affection and respect of his working comrades. His premature death has cut short his life in the plenitude of his powers.

V.M. Rodionov, N.N. Vorozhtsov, A.F. Smirnova,
L.A. Shchetinina,
A.P. Shestov, A.I. Korolev, V.O. Lukashevich,
V.N. Ufimtsev

IN MEMORY OF [illegible]

On October 27, 1969, after a long and serious illness, [illegible] central laboratory of the Dzerzhinsky [illegible] [illegible] Scientific Research Institute for Intermediates and Dyes, [illegible] aniline dye industry.

[illegible] was born in [illegible] [illegible] engineering technology [illegible] central laboratory [illegible] as a basis for the [illegible] was introduced for the first time in our industry.

Among a number of researches on the larger scale [illegible] attention should be made of the development of [illegible] and anthraquinone dyes.

We must also not overlook the great [illegible]

Under the direction of [illegible] with a large collective [illegible] State Prize in 1951.

The economic effect of the results of [illegible] millions of rubles.

Since [illegible] was a member of the Communist Party [illegible] awarded with the Order of [illegible] "In Memory of [illegible]"

[illegible] was a modest and sympathetic man and won the affection and respect of all [illegible]

[illegible]

THE PERIODIC LAW OF D. I. MENDELEEV AS A BASIC CONCEPT IN MODERN CHEMISTRY

(On the 85th Anniversary of the Discovery of the Law)

S. A. Shchukarev

D. I. Mendeleev wrote [1]: "Periodic relations belong to elements and not to simple bodies, and it is very important that one taken heed of this; . . . the physical properties are determined for the most part by the properties of the particles, and depend only indirectly upon the properties of the atoms which go to make up the particles. Because of this fact periods which are clearly and distinctly expressed, for example in the form of compounds, are already complicated in their physical properties.

"The properties of simple and of complex bodies are in periodic relation to the atomic weights of the elements only for the reason that the properties of simple and of complex bodies are themselves the results of the properties of the elements which make them up."

It is now clear that the main periodicity in properties of uncombined atoms, which depends upon properties of the electrons and their interactions with one another and with the atomic nucleus, is further complicated by formation of molecules and condensed phases as the result of chemical bond formation, as well as by the effects of quantum-statistical and thermodynamic factors. However, despite such complication, there is evident in an overwhelming majority of cases, most clearly, and with utmost surety, a periodic law for the properties of chemical compounds.

Back in 1871, D. I. Mendeleev, in the conclusion of his first edition of "Principles of Chemistry", wrote: "A major concern of chemistry is a study of the basic properties of the elements, since their properties are not completely known to us, and since up till now we have developed precise knowledge of but two . . . measurable properties, namely, the ability to produce known types of compounds, and that property known as the weight of an atom, which, therefore, leaves but one route open for development of extensive knowledge of the elements, which is a comparative study of the elements based upon the two-mentioned properties."

The present position of science has changed, in relation to which fact, teaching of the Periodic Law has acquired a new development and application; in particular, a knowledge of spectral and ionization studies for an overwhelming majority of the elements in connection with formulas for electronic configurations of neutral and charged atoms, gives such a meaningful and profound picture of periodicity in properties of electronic shells, that such picture ought to be given priority in contrasting chemical compounds with respect to primary aspects of the Periodic Law.

In substance, the condition is dependent upon the partner (oxygen, hydrogen), and in individual cases even appears to be thermodynamically unstable (MgH_2, AlH_3, Bi_2O_5, F_2O_7), and hardly characteristic for the given element (K_2O), or failing to correspond to the group number (Fe_2O_3, NiO, etc.); it is, therefore, natural to look for identical characteristics for an external electronic layer in free (neutral and charged) atoms with respect to both normal electronic configurations for the element and with respect to activated values connected with such configurations.

By no means is there an opportunity in the present article to discuss systematically and fully even the most fundamental concepts of the problem of spectral therm periodicity, and so we shall limit ourselves to an examination of only one problem which is of interest to chemists, namely, certain characteristics of periodicity of the principal ionization potentials of elements as related to the so-called secondary periodicity of heats of formation of binary chemical compounds. Thus, we shall illustrate a profound thought of D. I. Mendeleev regarding the transition from Periodic Law which characterizes the system of elements to the laws of chemical compounds.

Under the term secondary periodicity of ionization potentials we shall agree to include the following type of phenomena. It is known that in the fourth period of the system, the transition from K to Cu and from Ca to Zn correspond in first ionization potential to 3.4 and 3.1 eV; such increases depend upon the fact that the 4s- and $4s^2$-electrons drop into the more completely filled screen of 3d-electrons which are equivalent to each other, as the result of which the effective nuclear charge increases,which attracts the external electrons of the atoms.

For the fifth period, transitions from Rb to Ag and from Sr to Cd, for similar reasons, produce an increase in ionization potential of 3.4 and 3.3 eV, respectively; however, sixth period transitions from Cs to Au and from Ba to Hg correspond to considerably larger increases, namely, 5.36 and 5.2 eV, because in this case the $6s^2$-electrons drop not only into the 5d-screen, but also into the 4f-screen consisting of 14 electrons.

The elements prior to the lanthanides, and particularly the series from Hf to Hg, do not possess particularly large ionization potentials, according to the picture presented.

Strengthening of s-electron bonds, which depends upon dropping into the d- and f-orbitals, is the basis for that difference which we see in the properties of both sub-groups of the first and second groups of the system.

Thus, primary ionization potentials for Cu and Zn exceed considerably the K and Ca potentials; the primary potentials for Ag and Cd on the other hand, are somewhat smaller than the primary potentials of Cu and Zn, due to an increase in the principal quantum-number for the s-electrons torn off. Transition from Ag and Cd to Au and Ag again leads to an increase in primary potential because of additional f-consolidation.

Thus appears an important development of a non-repetitive order of primary potentials for the series:

I group Li, Na, Cu, Ag, Au;
II group Be, Mg, Zn, Cd, Hg.

For the same reason, course of the second is non-repetitive — as well as the s-potential for the indicated series of elements of the second group (Table 1).

TABLE 1

Ionization potentials	Elements				
	Li	Na	Cu	Ag	Au
I_I	5.37	5.09	7.67	7.59	9.22
	Be	Mg	Zn	Cd	Hg
I_I	9.30	7.63	9.37	8.96	10.38
I_{II}	18.12	15.10	18.04	16.80	18.80
$I_I + I_{II}$	27.42	22.73	27.41	25.76	29.18

Thus, the primary ionization potentials in the main sub-group of Group III correspond to tearing off of p-electrons, and therefore, correspond to non-repetitive course to a lesser extent, despite the fact that Ga, In and Tl, as well as Zn, Cd and Hg, proceed to take on d-electrons (and in the base of Hg and Tl, f-electrons in addition).

The course of I and I_{III}, as well as the sum of the three ionization potentials, is again markedly non-repetitive because the second and third electrons split off from the s-orbit (Table 2).

TABLE 2

Ionization potentials	Elements				
	B	Al	Ga	In	Tl
I_I	7.28	5.94	5.97	5.76	6.07
I_{II}	24.99	18.85	20.39	18.76	20.4
I_{III}	37.70	28.95	30.66	27.85	29.8
$I_I + I_{II} + I_{III}$	69.97	53.74	57.02	52.37	56.27

A very similar picture is also observed in the sub-groups:

C, Si, Ge, Sn, Pb,
N, P, As, Sb, Bi,
O, S, Se, Te, Po,
F, Cl, Bi, I, At.

Also, in those cases where potential is concerned, (the potentials whose number corresponds to the group number, or is one less than this group number), the s-electrons begin to participate in the orbits of chemical compounds, these s-electrons projecting themselves under the screen made of ten d-electrons (and sometimes made with an additional 14 f-electrons), as the result of which there appears a marked non-uniformity. Potentials of lower values (p-potentials) display non-uniformity not at all, or very poorly, increases simply being displaced by sharper decreases.

Sub-groups:

K, Rb, Cs, Fr,
Ca, Sr, Ba, Ra,
Sc, Y, La, Ac,
Ti, Zr, Hf, –,
V, Nb, Ta, –,
Cr, Mo, W, –,
Mn, Tc, Re, –,
Fe, Ru, Os, –,
Co, Rh, Ir, –,
Ni, Pd, Pt, –,

i.e., a series of elements whose potentials correspond either to rupture of s-electrons for construction of the d-screen, or to rupture of d-electrons themselves, are not related to the marked non-uniformity discussed here. For illustration, the authors have presented Fig. 1 for summated potentials of the principal and additional sub-groups of I, II, III and IV group elements.

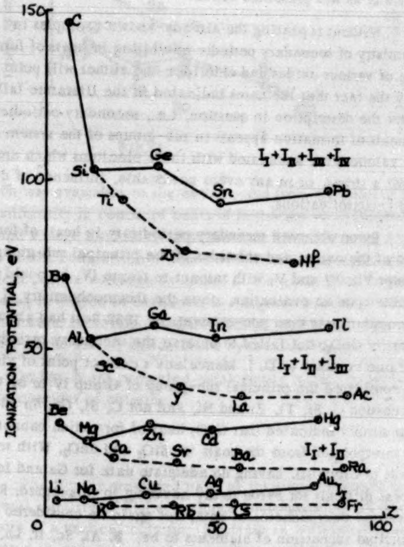

Fig. 1.

The above-discussed non-uniform, zig-zag course for individual potentials (equal in value to the number of the group of elements, or one less than the group number) can be designated secondary periodicity – in distinction to the principal periodicity which characterizes all elements series which are distributed without gaps in order of nuclear charges, secondary periodicity being evident upon examining the group lines which bind only elements of specific groups in the system.

Thus, in Fig. 2, with its characteristically classical principal periodicity, indicated by solid lines, dotted grouping lines can be seen; in this case, secondary periodic non-uniform lines for the first potential will be only lines for the series:

Li, Na, Cu, Ag, Au;
Be, Mg, Zn, Cd, Hg.

Similar graphs can be plotted for any potential, for example, in Fig. 2, the author presents a picture of the third potentials, on which the grouping lines for the sub-groups are the secondary periodics:

B, Al, Ga, In, Tl;
C, Si, Ge, Sn, Pb.

If an obligatory non-uniformity is not required for the course of the grouping lines, and alternation of steeper and more sloping sections is satisfactory, then the phenomenon can, of course, be observed in other sub-groups. In such more general form, it is better not to use the term "secondary periodicity", but simply to talk about the phenomena of d- and f-consolidations of the electronic bond (mainly of the s- and p-electrons, and to some extent of the d-electrons).

D. I. Mendeleev realized clearly that changes in properties of the elements in vertical columns of the Table can occur non-uniformly in a number of cases, thus interfering with interpolation and prediction of the properties of undiscovered elements, as the result of which he worked out such predictions by averaging values along not only the vertical, but along the horizontal as well, i.e., by crosswise utilization of information about the properties of the four neighboring elements.

Later, Byron [2] drew particular attention to the non-uniformity of modified properties of related chemical compounds from the principal sub-groups V, VI, and VII elements of the system, and termed this phenomenon secondary periodicity. Lately the phenomenon of non-uniformity in properties of chemical compounds for some groups of the system has been of interest to a large number of investigators: Rott [3], Kapustinsky [4], Balarev [5] and Shishokin [6]; foreign scientists have forgotten the existence of Byron's classical work.

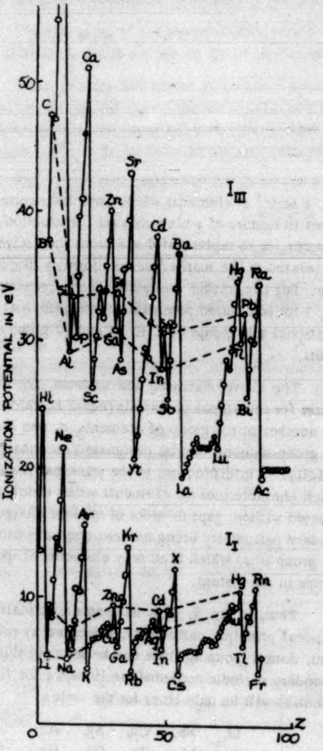

Fig. 2.

Now turning to the question of causes for the existence of a non-uniform course in properties of chemical compounds, the authors have assumed that secondary periodicity in properties of chemical compounds — which is complicated by thermodynamic and chemical interactions — can be explained as a reflection of secondary periodicity in electronic characteristics of the free electronic shells of the atom, in the general way as was presented above.

Without repeating the already-known examples in chemistry of secondary periodic exhibition in heats of formation of various oxides and chlorides, the author will point out only the fact that the cases indicated in the literature fall under the description in question, i.e., secondary periodicity in heats of formation appears in sub-groups of the system and the valences are associated with those electrons which are under a strong, or in any event noticeable, influence of d- and f-consolidations.

Byron observed secondary periodicity in heats of formation of the oxides and chlorides of the principal sub-groups of groups VII, VI and V; with respect to Group IV, he could not decide upon an evaluation, since the thermochemistry of germanium was then non-existent; by 1932 Rott had already data for GeO_2, but failed to observe the secondary periodicity, because contrary to D. I. Mendeleev's correct point of view, he considered the principal sub-group of Group IV to be the succession C, Si, Ti, Zr and Hf, and not C, Si, Ge, Sn and Pb. Rott simply indicated that GeO_2 heat of formation cannot be interpolated from the heats for SiO_2 and SnO_2. With regards to Group III, having no adequate data for Ga and In, it was difficult for Byron to say anything in this regard; Rott possessed thermochemical data, but again he considered the principal succession of elements to be: B, Al, Sc, It, La, and therefore did not notice anything, except for the heat of formation of Ga_2O_3 which could not be interpolated from the heats for Al_2O_3 and In_2O_3.

In order to enlarge information regarding secondary periodicity phenomena for the tetravalent states of the sub-group for Group IV elements, the author, along with Vasilkova, undertook a study of the heats of formation for compounds of these elements with magnesium. The investigation, which was completed in 1949, indicated [7] that these heats change non-uniformly upon transition from element to element, as was to be expected. Following this investigation, the author, together with Arya and Lakhtin [8], studied heats of formation for magnides of trivalent compounds of the principal sub-group of Group V, for which non-uniformity was again found — and this despite the fact that in such cases the valence electrons were not s, but p; d- and f-consolidations of the atoms, however, were found sufficient to be reflected in the heats of formation of the compounds. For comparison of non-uniform functions found by the authors with standard uniform course of heats of formation for magnesium compounds with elements of Groups VII, VI, V and IV, the heats of formation calculated per gram-atomic-weight of magnesium are compared in Fig. 3. As can be seen from Fig. 3, heats of formation of silicide and phosphide, of stannide and stibnide, of plumbide and bismuthide, approximate each other in pairs. Discrepancy in the case of germanide and arsenide is perhaps connected with lower accuracy in determination, because of the small amount of germanium which was available to the authors, and from the indefiniteness of heat formation for arsine. To illustrate the rule of uniformity in course of heats of formation for compounds of the main sub-groups of the elements, there can be quoted a large amount of experimental material, using literature data. Thus is produced a very informative picture on the comparison of heats of formation for higher oxides of various elements. There can be seen in Fig. 4 a typical picture variance in course of the group lines for the main and the sub-groups. Since compounds corresponding in degree of oxidation to the group number display secondary periodicity with particular clarity, higher oxides were, therefore, used as much as possible for Fig. 4. Values for heats of formation were, before plotting points on the graph, standardized by recalculating to 1 gram equivalent of oxygen.

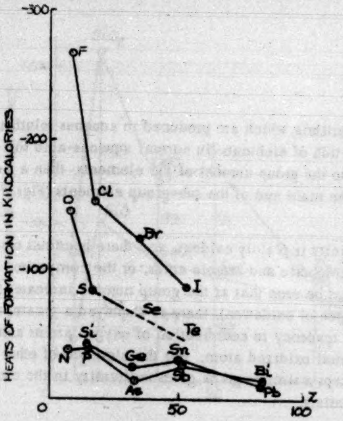

Fig. 3.

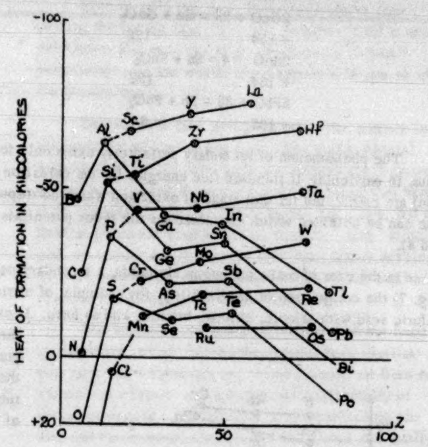

Fig. 4.

In Fig. 5 are presented (analogously to Fig. 4) heats of formation for the chlorides, claculated to 1 gram atomic weight of chlorine.

The figures presented have an important value in understanding two long-known rules concerning changes in thermal stability of higher-valence compounds for sub-groups of the system of elements in transition from top to bottom of a vertical column. Decrease in uniformity of ionization potentials for minor sub-groups, related to an increase in principal quantum numbers, results in a consolidation of higher-valency compounds when moving from top to bottom in the system. Thus, for example, WO_3 is more stable than CrO_3, WCl_6 exists, and Cr gives, with difficulty, $CrCl_4$; Re_2O_7 is more stable than Mn_2O_7, OsO_4 exists, and FeO_4 is not formed; so forth.

Secondary periodicity of ionization potentials in the main sub-groups produces a reverse situation for higher oxides of the main sub-groups; as a result, Bi_2O_5 does not form, PbO_2 is a strong oxidant similar to Tl_2O_3; HgO is less stable than ZnO, the gold oxides are less stable than the copper oxides.

For the same reason, As_2O_5, and especially SeO_3, are found to be strong oxidants, while higher oxides of fluorine and bromine are not yet known.

Difference in display of secondary periodicity by higher and lower oxides is readily seen in the case of main sub-groups elements of Group IV, which is indicated in the course of their heats of formation (Q for one gram formula weight) which is presented in Fig. 6. Because of secondary periodicity in heats of formation of higher oxides, the lower oxides, GeO and PbO are rendered stable, and are not inclined to a separation reaction to dioxide and the free element, while CO, SiO and SnO are capable of exothermal reaction (disproportionation).

In actuality: $2CO - 40 = C + CO_2$

$+54 \qquad -94$

$2SiO - 8 = Si + SiO_2$

$+200 \qquad -208$

$2GeO + 28 = Ge + GeO_2$

$+154 \qquad -126$

$2SnO - 4 = Sn + SnO_2$

$+134 \qquad -138$

$2PbO + 38 = Pb + PbO_2$

$+102 \qquad -64$

The phenomenon of secondary periodicity exists only for equilibria which are produced in aqueous solutions. Thus, in particular, if standard free energies for the oxidation reaction of elements (in normal aqueous-acid solution) are calculated for that stage of oxidation which corresponds to the group number of the elements, then a picture can be obtained which characterizes the redox potentials of the main and of the sub-group elements (Figs. 7 and 8).

In the case of main sub-group elements, a secondary periodicity is plainly evident, and there becomes clear (Fig. 7) the comparison of oxidizability, for example, of nitric, phosphoric and arsenic acids, or the comparison of sulfuric acid with selenic, chloric, bromic, and so forth. It can also be seen that as the group number increases (i.e., the degree of oxidation), there is displayed a greater and greater tendency to coordination of oxygen atoms around the central oxidized atom. For the elements of other sub-groups a similar graph gives uniformity in the course of potentials.

In light of the above situation, there becomes particularly evident the power of application, which was utilized by D. I. Mendeleev for prediction of the properties of gallium and germanium compounds, whose quantitative characteristics, on the basis of secondary periodicity, diverge noticeably from the average values between aluminum and indium, silicon and tin; with respect to scandium, prediction was easier since it lies in the sub-group, and the transition of Al—Sc—Y is more uniform than for the series Al—Ga—In.

In fact, the arithmetic mean of heats of formation of Al and In oxides is equal to 310 kcal, and for Ga has a heat of formation equal to 256 kcal; the average values for heats of formation of Al and Y oxides is equal to 410 kcal, and Sc also 410 kcal.

In individual cases of secondary periodicity, we can see how profound and in what detail the principal of periodicity of properties plays a role with respect to atomic electronic shells and the properties of chemical compounds. Both energy of crystalline structures and of gaseous molecules (ionic and covalent bonds), as well as energy of ion hydration (monoatomic or even polyatomic hydrolysis products, or complex formation) changes systematically on the whole with the sum of the ionization potentials, which correspond to specific degrees of oxidation. Depending upon whether the change in potential sum occurs more sharply or less so, than the change in corresponding energies for the lattice hydration energies, the heats of formation of the compounds and their heats of dissolution (in dilute solutions) change adiabatically or isothermally with the potential sums, in other words, by one way or the other, their periodicity is not only repeated in a general form, but also in more minute details. The situation is, of course, complicated with increase in the temperature, and often with ordinary temperatures in solutions, when entropy and temperature factors begin to play an important role, which are not considered from the viewpoint of periodicity in ionization potentials.

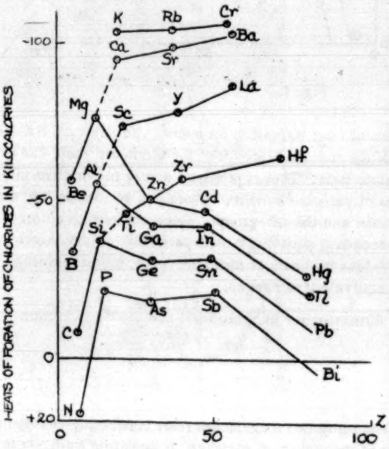

Fig. 5.

Without doubt, chemistry stands on the threshold of a course of investigation into periodicity of enthalpy, and even more so of free energies of formation for even the most simple compounds. The fact of periodicity itself, and a display of its most important details, for example of secondary periodicity, is well-known to us at present, but the real functional relationships which should be expressed in mathematical form remain a closed chapter.

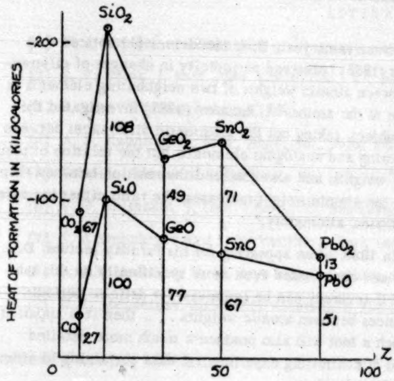

Fig. 6.

Back in 1871 [9], D. I. Mendeleev wrote concerning the known law: ". . . the function itself is not yet known, and only one of its properties is known — periodicity"; on the whole, this expression is true up to the present day.

Despite such slow development of the science in the direction of finding a quantitative mathematical expression of the Periodic Law, our esteem for it grows, and we are coming to increasingly understand that here is an outstanding law, and perhaps not just a law, but a general principle of periodicity, if by the term "principle" we understand it to mean that from which develop, as individual cases, many standard laws which can be expressed in concrete mathematical terms.

The Periodic Law should be considered the basis of chemistry, which defines the intermittent, qualitative modifications which accompany transition from one element to another, and which asserts periodicity of same, depending upon behavior of the combining nuclei and the external electrons of the atoms and qualitative changes in the series of elements arranged in order of increasing nuclear charge from hydrogen to centurium.

The D. I. Mendeleev Periodic Law is not expressed by an continuous, functional relationship; apparently, it cannot be completely characterized by any one general mathematical formula, because it is found to be a general and basic principle which possesses an infinite number of individual cases, which can, it is hoped, only be approached by experiment and mathematics.

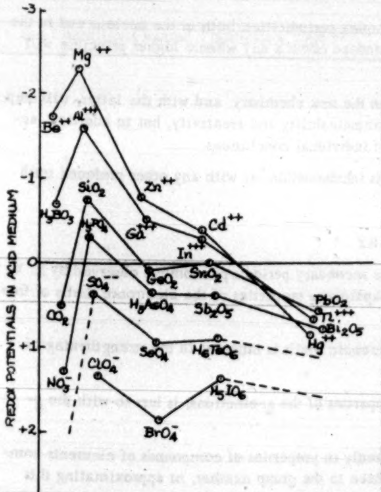

Fig. 7.

Touching only in a very general way upon the philosophical principal of transition from quantity to quality, let us apply the Periodic Law, as a scientific principle, to the specific system of qualitative characterization of the elements, i.e., let it be related to the behavior of free atoms; its individual expressions are varied and numerous, and applicable to the elements or chemical compounds each in a characteristic modified and complex form. Each specific case, therefore, should be related to periodicity of some specific physical or chemical property and its quantitative characteristics measured by experiment. Mathematical expressions of this law in such specific instances will, of course, be different.

The periodic principle laid down for electronic shells of the atom systems, intimately related to the ideas of saturation capacity of the shells and pairing of the electrons, has developed for chemistry a fundamental significance similar to the principles of quantum statistics and thermodynamic concepts of entropy and temperature for polyatomic systems, and to the principle of conservation of mass and energy for all of matter. The superposition of thermodynamic principles upon the periodic principle of D. I. Mendeleev, however, should produce true laws governing the formation, stability, and conversion of elements and chemical compounds; the author has in mind those laws which are closely associated with the ideas of saturation, coupling and substitution, to which D. I. Mendeleev gave so much attention in his chemical approach.

It is well-known that D. I. Mendeleev, in his classical formulation of the Periodic Law, compared forms of the compounds with atomic weights of the elements. In 1889, he wrote [1] thus: "To explain and to express the Periodic Law means to explain and to express the cause of the law of multiple relationships, differences in the elements, and changes in their atomic structure, and at the same time, requires an understanding of what is meant by mass and attraction." Thus, it can be clearly seen that D. I. Mendeleev actually placed before science two problems which, in modern terminology, can now be expressed as the problem of the nature of electronic shells and the nature of atomic nuclei.

In the same year, D. I. Mendeleev [1] noticed that Ridberg (1885) "observed periodicity in changes of differences between atomic weights of two neighboring elements in relation to the atoms. A. Bazarov (1887) investigated the same subject, taking not the arithmetic differences between neighboring and analogous elements, but the relation of their atomic weights, and also observed the relation between them that as the atomic weight increases, the ratio either increases or decreases, alternately."

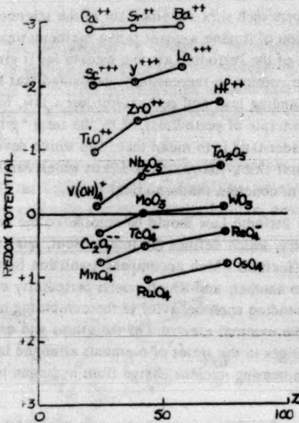

Fig. 8.

In 1889, when appearing for his Faraday lecture, D. I. Mendeleev commented even more specifically on this subject: "If accuracy can be improved for definite periodic differences between atomic weights. . . ., then it is apparent that such a tool will also produce a much more detailed method of controlling experimental data pertaining to atomic weight values".

At the present time, the idea of nuclear periodicity is universally recognized and has been developed extensively by many authors.

In 1889, D. I. Mendeleev wrote [1]: "Periodic change in simple and complex bodies is subject to some higher law, concerning which nature and cause there are, today, no means for grasping. In all probability, it is hidden in the fundamental beginnings of internal mechanism of atoms and particles."

Taking into account the existence of independent and complex periodicities, both in the nucleus and in the electronic shells of the atom, it can be assumed that there will indeed come a day when a higher principle will be found which will embrace both periodicities.

The old, titanic ideas of a great Russian chemist live on in the new chemistry, and with the latter, will step over into future centuries, retaining not only the brilliance, communicability and creativity, but in addition, acquiring newer meanings, and unfolding in an infinite diversity of individual conclusions.

The periodicity principle discovered by D. I. Mendeleev is inexhaustible, as with any other profound truth of the material world.

SUMMARY

1. It has been demonstrated in the present article that the secondary periodic phenomena observed by E. V. Byron for properties of chemical compounds are a reflection of analogous properties of the electronic shells of free atoms of the chemical elements.

2. The cause of secondary periodicity residing in the electronic shells is inherent in the strengthening of d- and f-electron valence bonds.

3. The indicated strengthening is most evident in the properties of the s-electrons, is less so with the p-electrons, and still less for d-electrons.

4. The result of secondary periodicity appears most markedly in properties of compounds of elements composing the main sub-groups of the system, corresponding in valence to the group number, or approximating this value.

5. Specific rules for the pattern of change in thermal stability of higher-valence compounds in sub-groups of the system are dependent upon secondary periodicity.

6. Secondary periodicity appears not only for the heats of formation of chemically-pure compounds, but also for redox potentials in aqueous solutions.

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* See Consultants Bureau Translation, page 929.

COMPLEX FORMATION OF THE ANION TYPE, BETWEEN POTASSIUM AND SODIUM PYROPHOSPHATES AND OXIDE SALTS OF THE TYPE MeO_4'' (Me=S, Mo, Cr, W)

A. G. Bergman and M. L. Sholokhovich

Complex formation between salts with common anions (cation complexes), for example $KCl \cdot MgCl_2 = K[MgCl_3]$, have up to the present time received considerably more study than complexes of the anion type, formed from salts with a common cation and with different anions, for example, $AgNO_3 \cdot AgCl$, $BaF_2 \cdot BaCl_2$.

A systematic investigation of mutual systems wherein are found two different cations with the same common anion, and two others with the same common cation, has led to an accumulation of interesting material on anion complexes.

At the present time a large number of anionic complexes have been obtained, among which many are characterized by sharply marked maxima on the melting point curves, with rather high melting points, as for example, $BaF_2 \cdot BaCl_2$ 1008°; its heat of formation was 15.1 kcal [1]. It has been considered up to the present time that complex formation is much more pronounced between potassium salts and other metals with common anions than for corresponding sodium salts.

Data given in the present article from an investigation of eight binary systems, as well as collected, extensive experimental material on the chemistry of molten salts, have shown a number of cases where the sodium salt displays a greater tendency to complex formation than the corresponding potassium salts.

TABLE 1

1st column = mol % of $K_4P_2O_7$; 2nd column = temperature at which first crystals appeared (E = eutectic)

1	2	1	2	1	2	1	2
$(K_2SO_4)_2-K_4P_2O_7$		$(K_2WO_4)_2-K_4P_2O_7$		$(K_2CrO_4)_2-K_4P_2O_7$		$K_4P_2O_7-(K_2MoO_4)_2$	
0	1070	0	928	0	984	0	1095
15	1040	6	916	12	948	20	1018
25	1018	12	904	18	930	25	995
35	992	18	888	24	920	30	982
40	976	23	870	30	902	32	968
45	962	27	862	35	890	35	956
50	934	31	848	40	876	40	932
55	898	33	840	42	880	45	910
60	898	36	852	45	888	50	886
65	936	39	869	50	906	55	866
70	960	45	904	55	920	60	845
75	996	50	930	60	936	62	830
80	1018	54	946	65	952	65	824
85	1046	57	960	70	968	70	842
				75	986	75	854
				80	1006	80	870
				85	1024	85	888
				90	1045	90	898
						95	911
E at 57.5% $K_4P_2O_7$ and 882°		E at 39% $K_4P_2O_7$ and 836°		E at 40% $K_4P_2O_7$ and 876°		E at 64% $K_4P_2O_7$ and 822°	

In Tables 1 and 2, and in Figs. 1 and 2 are given results of investigation of eight binary systems, of which four were formed from potassium pyrophosphate with potassium sulfate, chromate, molybdate and wolframate (Fig. 1), and the corresponding four – from analogous sodium salts (Fig. 2). Experimental data given in the tables indicated are incomplete for the sake of brevity.

TABLE 2

1st column= mol % of $Na_4P_2O_7$; 2nd column= temperature at which first crystals appeared (E = eutectic; P = transition point)

$(Na_2CrO_4)_2-Na_4P_2O_7$

1	2
0	816
6	787
9	777
12	765
18	806
21	838
24	853
27	875
30	903
33	916
36	914
39	912
42	912
45	903
48	886
51	875
54	866
57	853
60	847
63	866
70	916
75	934

E_1 at 12% $Na_4P_2O_7$ and 765°

E_2 at 59.5% $Na_4P_2O_7$ and 833°

$(Na_2MoO_4)_2-Na_4P_2O_7$

1	2
0	690
3	684
6	674
9	663
11	663
13	684
15	714
17.5	732
21	756
24	774
27	786
30	796
35	810
40	818
45	819
48	819
50	820
52	816
57	826
66	865
75	906
85	946
90	966

E_1 at 10% $Na_4P_2O_7$ and 654°

E_2 at 54% $Na_4P_2O_7$ and 807°

$(Na_2WO_4)_2-Na_4P_2O_7$

1	2
0	694
6	676
9	666
12	656
15	647
18	675
21	706
24	720
27	730
30	740
33	751
36	758
39	764
43	778
45	788
48	808
50	818
57	848
64	880
70	898
78	928
88	960

E at 15% $Na_4P_2O_7$ and 647°

P at 42% $Na_4P_2O_7$ and 767°

$Na_4P_2O_7-Na_2SO_4$

1	2
0	999
16	946
22	926
28	898
31	880
35	866
37.5	852
40	840
43	828
49	794
52	780
55	763
58	748
61	760
64	770
67	781
70	793
73	803
76	814
79	824
82	834
86	846
88	851
91	866

E at 58% Na_2SO_4 and 748°

It follows from the data obtained that the four binary systems formed by potassium pyrophosphate represent special eutectic systems, without complex formation on the liquidus curves. Subsequent investigation by thermographic analysis of the solid state should render evident the presence or absence of chemical affinity in the solidus. For the system $Na_2SO_4-Na_4P_2O_7$, the melting curve indicated a eutectic, the solidus region should also have been in detail. With sodium chromate, molybdate and wolframate, sodium pyrophosphate formed the following compounds $Na_4P_2O_7 \cdot 4Na_2CrO_4$, melting without decomposition at 916°, $Na_4P_2O_7 \cdot 2Na_2MoO_4$, also melting without decomposition at 821° and $Na_4P_2O_7 \cdot 2Na_2WO_4$, melting without decomposition at 767°. Of the systems indicated, experimental difficulties arose only during an investigation of the system $(Na_2CrO_4)_2-Na_4P_2O_7$. In this case, the equilibrium state of the system was reached only during numerous heating and cooling processes.

In this connection, it was possible to successfully demonstrate chemical affinity in the system only by investigating the given system through the method of additives. Investigation of the system by the method of melting temperatures, determined by the first appearance of crystals, led to the same conclusion only after repeated cooling and heating of each compound.

It is interesting that for the series of systems with sodium and potassium fluorides, and with oxygen-containing sodium and potassium salts, there exists a reverse relationship in complex formation.

Potassium fluoride forms compounds (melting with decomposition) with potassium pyrophosphate, chromate [2], tetrabromate [3] and carbonate [4], whereas for the corresponding systems with sodium salts, simple eutectics are formed.

Sodium and potassium fluorides with the corresponding sulfates form compounds melting without decomposition $KF \cdot K_2SO_4$, m.p. 887° [5] and $NaF \cdot Na_2SO_4$ [5], melting at 781°. Replacing the sulfate ion by pyrophosphate, and the fluoride ion by MeO_4'' anions of the sixth group (SO_4'', CrO_4'', MoO_4'', WO_4''), eutectic systems are obtained for the potassium series, and for the corresponding sodium salts, systems of the compounds are formed.

There is also observed complex formation in varying degree with other combinations of potassium and sodium salts. Thus, potassium nitrate and acetate form compounds melting without decomposition at 238°, whereas the corresponding sodium salts do not form such [6].

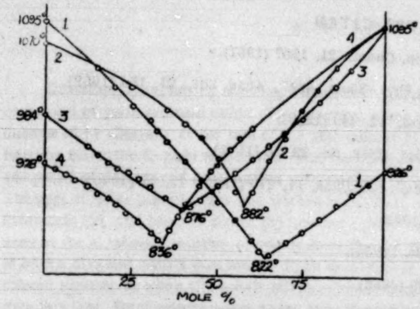

Fig. 1. Melting curves for the binary system: potassium pyrophosphate. 1) otassium molybdate; 2) potassium sulfate; 3) potassium chromate; 4) potassium wolframate.

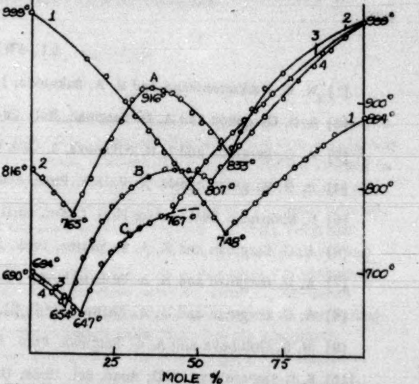

Fig. 2. Melting curves for the binary system sodium pyrophosphate –: 1) sodium sulfate; 2) sodium chromate; 3) sodium wolframate; 4) sodium molybdate.

A) $Na_4P_2O_7 \cdot 4Na_2Cr_2O_4$; B) $Na_4P_2O_7 \cdot 2Na_2MoO_4$; C) $Na_4P_2O_7 \cdot 2Na_2WO_4$.

On the other hand, sodium hydroxide and sodium nitrate form two compounds of the composition 2:1 and 1:1, melting without decomposition at 272° and at 271.5° [7], whereas KOH and KNO_3 give one compound of the composition 1:1, melting without decomposition, at 236.5°; note that KOH and KNO_3 have higher melting points (406 and 337°) than NaOH and $NaNO_3$ (320 and 308°). The same phenomenon is observed to a somewhat lesser extent for the alkali-nitrite systems. The compound $NaOH \cdot NaNO_2$ melts without decomposition at 206° [7] and $KOH \cdot KNO_2$ at 170° [7]; potassium nitrite melts at 436°, and $NaNO_2$ at 282°. This phenomenon is even more sharply evident between caustic alkalies and sodium potassium chromates: KOH and K_2CrO_4 form a eutectic system, and NaOH and Na_2CrO_4 form two compounds melting with decomposition [8].

The examples which have been quoted are already sufficient to demonstrate that the tendency to complex formation is not an innate property of any element by itself, but depends upon mutual relations between two salts (upon ionic radii and their general moments, upon external electronic shells, reciprocal polarization, and also upon that correlation which appears in formation of a crystalline lattice).

Moreover, the examples quoted confirm the status of chemistry of the molten salts which was established long ago, namely that the chemical properties of potassium and sodium differ considerably, and if there is a compound with similar type of sodium and potassium salts, that such is a coincidence rather than the rule. There are known a number of compounds characteristic only for sodium salts, or for potassium salts. Thus, for example, potassium salts form characteristic langbeinite complex $K_2SO_4 \cdot 2MgSO_4$ [9] (where instead of Mg, there can be Zn, Ni, Co, Mn, Pb), whereas sodium salts form the compound $3Na_2SO_4 \cdot MgSO_4$ and of composition $Na_2SO_4 \cdot 3MeSO_4$ [10]. These types of compounds are completely absent in potassium salts. Compounds of the composition 1:1 are also formed with sodium and potassium, but in aqueous solutions they produce a different series of the schoenite type $K_2SO_4 \cdot MeSO_4 \cdot 6H_2O$ (Me = Zn, Fe, Ni, Co), whereas sodium sulfate gives the astrakanite type $Na_2SO_4 \cdot MeSO_4 \cdot 4H_2O$. Further, we have the characteristic $KCl \cdot MgSO_4$ for the kainite type salt, where potassium can be replaced by Rb, Cs, Te, NH_4; Mg by Zn; Cl' by Br', and I' [11]. Sodium salts do not form complexes of the kainite type.

SUMMARY

1. By visual polythermic method, the following binary systems have been investigated: 1) $(Na_2SO_4)_2 - Na_4P_2O_7$; 2) $(Na_2CrO_4)_2 - Na_4P_2O_7$; 3) $(Na_2MoO_4)_2 - Na_4P_2O_7$; 4) $(Na_2WO_4)_2 - Na_4P_2O_7$; 5) $(K_2SO_4)_2 - Na_4P_2O_7$; 6) $(K_2CrO_4)_2 - K_4P_2O_7$; 7) $(K_2MoO_4)_2 - K_4P_2O_7$; 8) $(K_2WO_4)_2 - K_4P_2O_7$.

2. It has been established that for all systems where potassium salts participate, there is no complex formation.

3. In binary systems 1, 2 and 3, where sodium salts participate, compounds are formed, in contrast to similar systems where potassium salts participate.

4. The results obtained attest to profound differences in the chemical properties of sodium and potassium salts.

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* See Consultants Bureau Translation, page 2171.

COMPLEX FORMATION REACTION BETWEEN DIVALENT COBALT AND DIMETHYLGLYOXIME

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Dimethylglyoxime, by reacting with salts of divalent cobalt in neutral or alkaline medium, forms a soluble compound of yellow-brown color. This reaction, along with many other reactions of α-dioximes with metals, was discovered by Chugaev at the turn of the 20th century [1]. It is known, however, that Chugaev did not succeed in isolating either the dioximine of simple form $Co(HDm)_2$ (HDm^-, monovalent dimethylglyoxime anion), or any other compound of determined composition with divalent cobalt, despite evidence of its formation in aqueous solution. Attempts of other investigators who worked in this field after Chugaev were also fruitless. In 1923, Feigl and Rubenstein [2], and later Peshkova [3] isolated a green compound of the composition $Co(H_2Dm)_2Cl_2$, by heating acetone (or alcoholic) solution of cobalt chloride with dimethylglyoxime, which for a long time was considered to be the divalent cobalt compound. Upon dissolving in water, this compound forms the same yellow-brown colored solution as when the cobalt salt is mixed with dimethylglyoxime under the usual conditions. Proceeding from this fact, Feigl assumed that at the base of soluble dioximines of cobalt oxide there lies the compound $Co(H_2Dm)_2X_2$, where X^- equals a monovalent acid radical, and H_2Dm equals the dimethylglyoxime molecule.

Quite a number of works have been dedicated to a study of the properties of the compound $Co(H_2Dm)_2Cl_2$. However, data referring to the properties of this compound, including the valencies of cobalt in it, have been contradictory, and deductions about the structure do not agree with classical concepts of Chugaev regarding the dioximine structure. On the other hand, there is no data in the literature concerning the complex formation reaction between divalent cobalt and dimethylglyoxime under the usual analytical conditions. Instances are known, however, where reaction with α-dioximes proceeds differently, depending upon the medium. Thus, for example, in anhydrous solvents (alcohol, acetone) copper forms with dimethylglyoxime an addition product of the composition $Cu(H_2Dm)Cl_2$ [4], and in aqueous solution, $Cu(HDm)_2$ [1].

In the present work, the authors have given results of an experimental study of the reaction between divalent cobalt and dimethylglyoxime.

EXPERIMENTAL

Synthesis and Analysis of the Compound $Co(H_2Dm)_2Cl_2$

The compound $Co(H_2Dm)_2Cl_2$ was prepared according to the method of Feigl by heating an acetone solution of cobalt chloride and dimethylglyoxime mixture taken in the mole ratio of 1:2 under reflux, for the purpose of studying its properties. It was found that the yield of crystal product was higher if the reaction mixture was not heated, but allowed to stand at ordinary temperature in an oven for 24 hours. The resulting compound was readily soluble in water, but upon acidification of the aqueous solution, again separated in the form of large, lustrous, dark-green crystals. This property was utilized for recrystallization. A saturated aqueous solution of the crude product was acidified with concentrated hydrochloric acid until the crystals had precipitated, which were then immediately filtered off, washed first several times with small portions of cold water, and then with acetone. After drying at 105°, the percentage composition of cobalt and of chlorine was determined. Cobalt was determined by gravimetric means as the hydrochloride after acidification of the organic residue from nitric acid and subsequent vaporization with sulfuric acid. For determination of chlorine, the batch was dissolved in water and the resulting solution heated almost to boiling, keeping in the heated stage for 30 minutes. After addition of silver nitrate, the mixture was cooled to 30-40°, and 20 ml of nitric acid, 1:10, then added. The mixture was stirred without heating to the complete coagulation of silver chloride. The procedure was then carried out as usual.

16.20% of cobalt was found and 18.95% of chlorine. Calculation carried out on the basis of analytical data (content of dimethylglyoxime by difference) gave for the components a ratio of Co : H_2Dm : Cl = 1:2:2, which corresponds to the data of Feigl, as well as that of Peshkova.

Properties of the Compound Synthesized from Acetone Solution

Feigl considers that for the given compound cobalt is divalent. His conclusionis based on the assumption that he obtained an identical compound in the presence of hydroxylamine as a reducing agent. In his opinion, the compound $Co(H_2Dm)_2Cl_2$ is an addition product, i.e., the acid radicals are ionically bound (reaction with silver nitrate), and two unchanged dimethylglyoxime molecules enter into the composition of the complex ion; $[Co(H_2Dm)_2]Cl_2$ groups, instead of the grouping adopted by Chugaev. The compound hydrolyzes in aqueous solution in accordance with the following scheme:

$$[Co(H_2Dm)_2]Cl_2 + H_2O \rightleftharpoons [Co(H_2Dm)_2](OH)Cl + HCl, \qquad (1)$$

which Feigl verifies only from analytical data for the hydrolysis product which precipitates when a saturated aqueous solution of $Co(H_2Dm)_2Cl_2$ is allowed to stand. Feigl does not furnish any other information concerning the properties of the green compound and its hydrolysis product. Feigl also refers $Co(H_2Dm)_2Br_2$ and $Co(H_2Dm)_2I_2$, to the same type of compound which he obtained according to the above-indicated method. Thiele and Heilborn [5] also limited themselves to a study of the individual properties of the green compound. They observed that when treating it with sulfuric acid, there was no evolution of hydrogen chloride, which should have taken place if chloride ions were present in the external medium. Proceeding from this fact, they proposed a structure with chlorine bound non-ionically: $[Co(H_2Dm)_2Cl_2]$. Heiber and Leutert [6] came to the same conclusion about the structure on the basis of a small electroconductivity value for the acetone solution. Indications are found in later works that the compound $Co(H_2Dm)_2Cl_2$, and its hydrolysis product, are similar to other complex compounds of trivalent cobalt, in that they are diamagnetic, and hence that trivalent cobalt, and not divalent, enters into the composition. In accordance with this deduction, it was found that a property of this green compound was release of iodine from an acidified solution of potassium iodide. Sen and Ray proposed an unlikely formula with asymmetric structure for the molecule $\left[Co^{III} \begin{matrix} HDm \\ H_2Dm \end{matrix} Cl_2 \right]$ [7].

Taking into account the possibility of divalent cobalt oxidizing to trivalent by oxygen of the air, during synthesis of the green compound, the authors carried out a control experiment in a sealed tube, the space over the reaction mixture having been filled with carbon dioxide. It was found that in the absence of air, reaction did not proceed, heated or not, even after several days. Only upon opening the tube did green crystals of the compound immediately begin to precipitate. This fact indicated that for the given case, a trivalent compound of cobalt was formed. The correctness of this deduction is confirmed by all of the peroperties exhibited by this compound in aqueous solution, wherein it displays close analogy with the properties for dioximine complexes of trivalent cobalt [8], rhodium [9] and iridium [10] which have already been extensively studied.

The green compound dissolves in water, alcohol, acetone, but is insoluble in ether. The solubility in water at 20° was equal to 2 g/100 ml; upon addition of alkali, it was noticeably increased.

An aqueous solution of the green compound has a strong acid reaction. Upon introducing hydrochloric, sulfuric or nitric acid, the initial substance results immediately. This phenomenon can be explained either by reversibility of the hydrolytic rupture of the complex, with isolation of the acid (equation 1), or by a decrease in solubility produced by introduction of common H^+ ions, if the dissolved substance is, itself, an acid.

On the strength of the above-indicated and other properties, similar to properties for the complex dioximine acids of trivalent metals which have already been described in the literature, the following formula might be proposed for the investigated compound: $H[Co(HDm)_2Cl_2]$. Confirmation of the accuracy of this deduction depends upon determination of the sign of the colored complex ion charge, a study of the reaction with silver nitrate, measurement of electroconductivity and pH, as well as conductometric titration of the solution with alkali.

To determine the charge of the complex particle, a solution of the investigated compound, with a small amount of added potassium chloride, was placed in the lower part of a U-shaped tube containing stopcocks. The space over the stopcocks was filled with potassium chloride solution of the same concentration as was taken for the lower solution. Under the effect of current, the limit of the colored layer was displaced toward the anode; according to the structure proposed by Feigl, a complex cation should have been formed. The reaction with silver nitrate is also very characteristic. Upon addition of silver nitrate to a freshly-prepared solution of the green compound, there immediately precipitated out a silver compound with the complex ion, in the form of a crystalline yellow precipitate, and not silver chloride, as indicated in the literature. The salt was poorly soluble in water, unstable, and upon heating decomposed rapidly, splitting out silver chloride. If the solution was first heated, and then silver nitrate added, chloride ions then precipitated out immediately (see above the method for determination of chlorine in this compound). The given experiments demonstrate the presence of a complex anion in the compound, into the composition of which chlorine atoms also enter. The latter are held very loosely in the internal sphere and under favorable conditions can be displaced by solvent molecules.

To determine the basicity of the acid. the pH for a series of freshly-prepared solutions (Table 1) was measured.

TABLE 1

pH of the Solution $H[Co(HDm)_2Cl_2]$

Solution No.	Concentration		pH	
	g/100 ml	mole /l.	measured	calculated
1	0.3661	$1 \cdot 10^{-2}$	1.95	2.0
2	0.1830	$5 \cdot 10^{-3}$	2.24	2.3
3	0.0366	$1 \cdot 10^{-3}$	2.84	3.0

Upon comparing the data of Table 1 it can be seen that the measured pH values are close to theory, calculating on the assumption that the compound studied is a strong monobasic acid. Monobasicity of the acid is confirmed also by measurement of the molar electroconductivity (μ = 280 ohm^{-1} cm^2 at V = 1000 and t = 22°) and by conductometric titration. There is shown in the figure a titration curve for 0.3661 g (0.001 mole) $H[Co(HDm)_2Cl_2]$ with 0.1 N alkali solution (ordinate axis equals resistance, abscissa axis equals milliliters of alkali added).

10 ml of alkali was used for titration.

The results given above give grounds for suggesting that in acetone solution $CoCl_2$ and dimethylglyoxime, in the presence of oxygen of the air, react according to the equation:

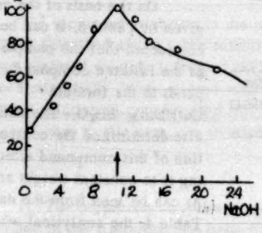
$$2CoCl_2 + 4H_2Dm + \tfrac{1}{2} O_2 = 2H[Co(HDm)_2Cl_2] + H_2O. \qquad (2)$$

The compound $H[Co(HDm)_2Cl_2]$ is thus found to be an analog of the dioximine acids of trivalent cobalt, rhodium and iridium ions.

The complex acid $H[Co(HDm)_2Cl_2]$in aqueous solution gradually reacts with the solvent, from which results a readily-crystallizing brown substance. Analytical results for it indicated the composition $[Co(HDm)_2ClH_2O]$. The substances contained, in percent: 17.30 cobalt, 10.11 chlorine. Theoretically calculated (in %): 17.15 cobalt, 10.31 chlorine.

The hydration process is reversible:

$$H[Co(HDm)_2Cl_2] + H_2O \rightleftharpoons [Co(HDm)_2Cl \cdot H_2O] + HCl. \qquad (3)$$



Curve for conductometric titration of $H[Co(HDm)_2Cl_2]$ with alkali.

Introduction of acids displaces the equilibrium from right to left.

The compound $[Co(HDm)_2 Cl \cdot H_2O]$ is hardly soluble in water; at 22° the solubility amounted to 0.17 g in 100 ml; negligible solubility in acetone, and almost insoluble in ether. Its freshly-prepared aqueous solution had a very low electroconductivity: μ = 3 ohm^{-1} cm^2 at V = = 1000 and t = 22°, which coincided with electroconductivity for the complex $[Co(HDm_2)NO_2H_2O]$, described in the works of Chugaev [8]. Electroconductivity increased with time. This was apparently related to "washing out" of the second coordinated chlorine ion from the internal sphere.

Apparently, the bromo- and iodo-derivatives $H[Co(HDm)_2Br_2]$, $H[Co(HDm)_2I_2]$ should also be related to the dioximine complex acids of trivalent cobalt, taken erroneously to be compounds of divalent cobalt by Feigl and others [2], as well as the compound which was isolated by Cambi from water-alcohol mixture of monomethylglyoxime with $CoBr_2$ in the presence of HBr [11].

Study of the Reaction Between the Divalent Cobalt Ion and Dimethylglyoxime in Aqueous Solution

The reaction between divalent cobalt and dimethylglyoxime in aqueous solution proceeds externally, in a manner analogous to cobalt in the nitroso-R-salt reaction. In acid medium the Co^{++} ions do not react with dimethylglyoxime. In weak acid medium, a yellow coloration appears which increases with increase of pH. If the initially alkaline solution is acidified, then the yellow color remains without apparent change. Irreversibility of the reaction makes it impossible to apply the method of physico-chemical analysis to a solution of this system.

With a mixture of Co^{++} and H_2Dm, with small excess of cobalt ions, nickel ions do not form the nickel dimethylglyoximine precipitate; consequently, dimethylglyoxime is retained by the cobalt ions more securely than by the nickel ions. The ratio of reacting components (Co^{++} and H_2Dm) in solution was determined as follows. A titrated alcoholic solution of dimethylglyoxime was added from a buret to a known amount of cobalt salt in weak acid solution (mixture of sodium acetate and acetic acid). A drop of the solution under investigation was periodically transferred to a strip of filter paper saturated with nickel salt. The amount of reagent used for complete binding of cobalt by the complex was determined by the formation of a red spot on the indicator paper. The results are given in Table 2.

TABLE 2

Ratio of Cobalt and Dimethylglyoxime Reacting in Aqueous Solution

0.1 M $CoCl_2$ solution taken (ml)	Medium	0.1 M H_2Dm used (ml)
4.0	Weak acid	8.2
5.0	Weak acid	10.1
6.7	Weak acid	13.5
4.0	Ammoniacal	8.3
6.0	Ammoniacal	12.3
8.0	Ammoniacal	16.2

It can be seen from Table 2 that in weak acid and ammoniacal solutions, cobalt reacts with dimethylglyoxime in the ratio of 1:2.

Isolation of Co^{II}-dimethylglyoximine and Its Analysis

Chugaev hypothesized formation of $Co(HDm)_2$ in aqueous solution. Even upon combining concentrated solutions of the cobalt salt with dimethylglyoxime (alcoholic or alkaline) the compound did not separate out. Further concentration of the solution did not lead to separation of a homogeneous reaction product, evidently due to formation of a mixture of compounds of di- and trivalent cobalt. For separation of the compound, the authors set up an experiment on the basis of some general properties of dioximines. Disodium dimethylglyoxime salt solution was added in the molar ratio of 1:2 to a cobalt salt solution. The resulting mixture was treated with dilute acid. As the alkali was neutralized a finely-crystalline yellow substance separated from solution, which was filtered off, washed with water, and dried in air. To study the properties, three preparations were made simultaneously, and the initial compound cobalt chloride, hydrochloride and nitrate were taken. Cl^-, $SO_4^{=}$ and NO_3^- ions were not found, in contrast to the above-described complex of trivalent cobalt. Upon holding the air-dried preparations in a drying compartment at 105°, the latter turned dark rapidly, and its decrease in weight was due to water loss. The percentage content of cobalt by gravimetric procedure was also determined in the form of $CoSO_4$ and nitrogen according to Kjeldahl,* as well as the water content.

Analytical results are given in Table 3.

TABLE 3

Analytical Results for Air-Dried Co^{II}-Dimethylglyoximine

Component determined	Determined in the preparation (%) from the chloride	from the hydrochloride	from the nitrate	Average	Calculated for $Co(HDm)_2 \cdot 8H_2O$
Water	34.20	34.24	34.05	34.10	33.27
Cobalt	14.26	14.05	13.92	14.07	13.62
Nitrogen	11.90	11.73	12.01	11.94	12.93

TABLE 4

Analytical Results for Co^{II}-Dimethylglyoximine, Dried to Constant Weight at 105°

Component determined	Determined in the preparation (%) from the chloride	from the hydrochloride	from the nitrate	Average	Calculated for $Co(HDm)_2$
Cobalt	20.12	20.49	20.43	20.34	20.38
Nitrogen	18.15	18.21	18.15	18.18	19.38

On the basis of the data given in Table 3, it can be considered that the composition of the isolated compound corresponds to the formula $Co(HDm)_2 \cdot 8H_2O$. The authors also determined the composition of this compound after drying it to constant weight at 105°. As can be seen from the data of Table 4, the analytical results confirm conclusions concerning the ratio Co : H_2Dm of the complex.

The preparation $Co(HDm)_2 \cdot 8H_2O$ at normal temperature was difficult to dissolve in water. Only upon prolonged contact with water (over 24 hours) did it gradually begin to dissolve, but failed to reach constant solubility. Upon heating, its solubility first increased; however, after cooling the solution, no solid phase appeared. Upon further cooling and boiling, the solution changed from its yellow color to red-brown and became turbid. Because of the extremely slow attainment of equilibrium, no accurate data on solubility were obtained. $Co(HDm)_2 \cdot 8H_2O$ dissolved in butyl, isobutyl, isoamyl alcohols and in pyridine; insoluble in alcohol, acetone, ether, toluene and xylene.

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* A certain inaccuracy in this method as applied to dioximines should be mentioned; the error in determining nitrogen is equal to about 1%. The authors have obtained the same error when determining nitrogen in nickel dimethylglyoximine, the composition of which was accurately determined.

As with palladium, platinum and copper dimethylglyoximines, containing water, Co^{II}-dimethylglyoximine (anhydrous) was readily soluble in alkali hydroxide, ammonia, sodium carbonate, sodium acetate. Upon neutralization of the alkaline solutions, crystal hydrates separated in both cases. From its cobalt content in the filtrate after 10 minutes saturation, the authors determined the solubility of $Co(HDm)_2 \cdot 8H_2O$ in alkali solutions of three concentrations (Table 5).

TABLE 5

Solubility of $Co(HDm)_2 \cdot 8H_2O$ in the Presence of NaOH

NaOH concentration (in moles/liter)	Solubility (in moles/liter)
$1 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$
$1 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
$1 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$

Solubility increased in proportion to the concentration of alkali, and was considerably higher than for the trivalent cobalt compound described above.

The solubility of dioximines in alkalies is evidently tied up with the presence in their molecules of two hydrogen atoms which have remained on the oxime groups. It is known [12] that dimethylglyoxime, when reacted with alkali, behaves as a dibasic acid, although a very weak one:

$$K_1 = \frac{[H^+][HDm^-]}{[H_2Dm]} = 8 \cdot 10^{-12} \text{ and } K_2 = \frac{[H^+][Dm^{--}]}{[HDm^-]} \approx 10^{-14}.$$

The dimethylglyoxime complexes with ions of divalent metals: Ni^{++}, Cu^{++}, Pd^{++}, Pt^{++}, Pt^{++}, $[Me^{II}(HDm)_2]$, are acid salts. On addition of alkali, the second hydrogen ion is apparently replaced by the alkali metal, with formation of an intermediate salt.

$$CO(HDm)_2 + 2OH^- = Co(Dm)_2^{--} + 2H_2O. \tag{4}$$

Formation of the complex anion in alkali solution was verified by electrolysis in a U-shaped tube, into the bottom part of which was poured the alkaline solution of Co^{II}-dimethylglyoximine in the presence of hydroxylamine. The side liquid was alkaline solution and hydroxylamine of the same concentrations. Upon electrolysis, the colored layer shifted toward the anode.

Co^{II}-Dimethylglyoximine (both aqueous and anhydrous), in distinction to nickel- and copper-dimethylglyoximines, dissolves in hydrochloric, sulfuric and nitric acids without decomposition (if the solution is not heated), forming yellow solutions. It can be isolated again from acid solution by careful neutralization of the acid with alkali.

The increased solubility in the presence of acid for this compound differs sharply from the trivalent cobalt complex described above. The solubility of Co^{II}-dimethylglyoximine increases greatly in concentrated HCl, and a green colored solution is formed, which is noticeably distinct from the color of the salts of divalent cobalt in concentrated HCl. When diluted with water, the yellow color returns. With short heating in air of the saturated complex solution in concentrated HCl green crystals separated. Analysis of this product, and qualitative analysis, indicated that in this case, the trivalent cobalt compound described above was formed.

SUMMARY

1. The properties of a dimethylglyoxime cobalt compound separating from acetone solution, which has been described in the literature, has been studied. It has been demonstrated that this compound, erroneously considered by a number of authors to be the divalent cobalt compound, has been found to be the trivalent cobalt compound. Based upon a study of the formation and properties of the compound in aqueous solution (pH, electroconductivity, charge on the colored complex ion, reaction with silver nitrate and others) it has been deduced that its structure is $H[Co(HDm)_2Cl_2]$. It has been demonstrated that the compound $H[Co(HDm)_2Cl_2]$ reacts in aqueous solution with the solvent to form the complex non-electrolyte $[Co(HDm)_2Cl \cdot H_2O]$.

2. The complex formation reaction between Co^{++} and H_2Dm in aqueous solution has been studied. In acetic and ammoniacal media, the components react in the ratio of 1:2. The complex formed is more stable than nickel dimethylglyoximine. By the method of neutralizing a mixture of solutions of the divalent cobalt salt and the disodium salt of dimethylglyoximine with acid, the compound $Co(HDm)_2 \cdot 8H_2O$ has been isolated and a number of its properties studied.

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THE PROBLEM OF CAUSES FOR INHIBITION OF SYNTHESIS OF ALDEHYDES AND CARBOXYLIC ACIDS BY THE CATALYTIC OXIDATION OF UNSATURATED HYDROCARBONS

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A number of investigations [1, 2] have been published in the literature, wherein attempts have been made to synthesize valuable organic compounds by the oxidation of aliphatic hydrocarbons with catalysts, and in particular, the synthesis of aldehydes and carboxylic acids by oxidation of individual unsaturated hydrocarbons (ethylene and propylene), as well as their mixtures in gases from petroleum cracking. In all of the works, yields of the aldehydes and acids were very small.

The purpose of the present work is a clarification of the origin and behavior of the intermediate products which appear in the oxidation process, using as an illustration the example of propylene oxidation by oxygen of the air. The authors used silver and vanadium catalyst, which is normally used for "soft" oxidation of hydrocarbons.

Oxidation was carried out by the usual flow-type arrangement. The reaction products were analyzed for total content of carboxylic acids by titration with 0.1 N KOH solution, and for total content of aldehydes, by the hydroxylamine procedure. Propylene, carbon dioxide, carbon monoxide and oxygen contents were determined by volumetric procedure using an apparatus of the Orsat type. The contact time was determined by the ratio of gas volume passed through to volume taken up by the catalyst.

In oxidation of propylene with the above-indicated catalysts, it can be presumed that aldehydes and carboxylic acids with 1 to 3 carbon atoms are formed as intermediate products.

TABLE 1

Homogeneous Oxidation of Propylene, Acetaldehyde and Acetic Acid

Experimental conditions		Composition of the initial mixture (in vol. %)				Composition of the reaction products (in vol. %)			Percentage conversion
temperature	contact time (secs)	C_3H_6	CH_3COH	CH_3COOH	O_2	initial organic compound	CO_2	aldehyde calculated for HCOH	
370°	5	2.4	–	–	20.0	2.0	0.8	0.05	16
278	3	2.4	–	–	20.0	2.1	0.6	0.14	12
400	1.4	3.0	–	–	20.0	2.9	0.2	Traces	Small
400	5	–	5.8	–	20.0	3.36	5.0	–	43
400	5	–	5.4	–	20.0	2.40	6.0	–	55
390	5	–	–	1.2	20.0	0.32	1.7	–	73
395	5	–	–	0.77	20.0	0.15	1.2	–	80
405	5	–	–	0.75	20.0	0.04	1.4	–	94

First of all, the possible role of homogeneous oxidation and thermal decomposition of not only propylene but also its possible products of incomplete combustion, should be evaluated; for the latter, acetaldehyde and acetic acid were used for the experiments. Experimental results of the oxidation are given in Table 1, from which data it can be seen that under the same conditions, propylene oxidizes homogeneously, and to a lesser extent, than does acetaldehyde or acetic acid.

It has been established in separate experiments that the substances indicated in Table 1 remain unchanged upon passage through, in admixture with nitrogen, at 400°. Thus, the complications associated with thermal decomposition are not be be feared; on the other hand, homogeneous oxidation can be a real complicating circumstance in a study of the catalytic oxidation of propylene with vanadium catalyst, which works in the range of relative high temperatures (400°).

Catalytic oxidation of propylene was first sudied with silver catalyst, with which the process became noticeable below 200°. Propylene was obtained by dehydration of isopropyl alcohol, which was exhaustively distilled on a fractionating column with efficiency corresponding to 40 theoretical plates. In these experiments temperature was varied from 200 to 250°, and the contact time from 4 to 45 seconds, and the oxygen content from 6.6 to 20%. The results obtained are given in Table 2.

TABLE 2

Propylene Oxidation on Silver

Experimental conditions		Composition of the initial mixture (vol. %)		Composition of the reaction products (in vol. %)					Percentage of conversion
temperature	contact time (secs.)	C_3H_6	O_2	aldehydes (qualitatively)	carboxylic acids (qualitatively)	propylene oxide (qualitatively)	C_3H_6	CO_2	
200°	10	1.6	20.0	None	None	Found	1.4	0.6	12.5
230	13	2.4	20.0				0	7.4	100
230	7	2.4	20.0				0	7.0	100
240	12	2.2	20.0				0	7.0	100
240	4	2.0	20.0				0.2	5.2	90
210	45	3.4	6.6	None	None	None	–	–	10
250	45	3.4	6.6				–	–	30

It follows from these experiments that upon oxidizing propylene on silver, there are found no aldehydes or acids at all, traces of propylene oxide, and a large amount of products of complete oxidation (CO_2). All three atoms of carbon are oxidized to carbon dioxide, i.e., a complete extensive oxidation of propylene occurs. To clarify the behavior of aldehyde on silver catalyst, an experiment was set up with formaldehyde, the latter being at 260° and for a contact time of 10 seconds, being passed over catalyst in mixture with air; in this case, no aldehyde was found in the reaction products, not even qualitatively, i.e., under such conditions, oxidation is complete.

Thus, in contrast with ethylene which oxidizes "softly" to ethylene oxide on silver catalyst, propylene oxidizes more extensively under the same conditions, and the process fails to stop at the intermediate phase by modification of experimental conditions.

TABLE 3

Propylene Oxidation on Vanadium Catalyst (V_2O_5) at 400°

Experimental conditions		Initial mixture (in vol. %)		Reaction products (in vol. %)						Yield of products (mol%)*				% conversion of C_3H_6	Time of catalyst work (hrs)
rate (liters per hour)	contact time (sec.)	C_3H_6	O_2	aldehydes	acids	CO_2	CO	C_3H_6	O_2	aldehydes	acids	CO_2	CO		
26	1.3	3.0	4.8	0.08	0.02	0.4	0.2	2.7	0.6	8.8	2.2	44.4	22.2	10	0.5
29	1.2	3.0	5.2	0.12	0.01	1.8	1.4	1.8	0.2	3.3	0.3	50.0	38.8	40	1.0
29	1.2	2.4	4.8	0.10	0.01	1.9	1.2	1.0	0.2	2.4	0.24	45.2	28.5	58	1.5
29	1.2	2.4	4.8	0.13	0.01	1.9	1.2	1.0	0.2	3.1	0.24	45.2	28.5	58	2.0
29	1.2	2.4	4.8	0.12	0.01	1.9	1.7	1.0	0	2.9	0.24	45.2	40.5	58	2.5
29	1.2	3.2	5.0	0.19	0.01	2.0	1.6	2.2	0.2	6.3	0.33	66.6	53.3	31	3.0
29	1.2	3.2	5.0	0.18	0.01	2.0	1.6	2.0	0.2	5.0	0.25	55.5	44.4	37	3.5
24	1.4	3.6	4.8	0.18	0.01	1.5	2.0	2.4	0	5.0	0.25	41.7	55.5	33	5.0

Oxidation of propylene was also studied by the authors over vanadium pentoxide. Small amounts of aldehydes and carboxylic acids were found among the reaction products, along with large amounts of carbon dioxide and carbon monoxide; experimental conditions were modified to increase yields of the aldehydes and carboxylic acids. It was established that optimal conditions are: a temperature of 400°, a contact time of about 1 second and an oxygen content below the stoichiometric. A series of experiments carried out under optimal conditions are shown in Table 3.

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* With respect to theoretical yield, calculated on the basis of propylene converted. Sum of reaction products is not equal to 100% because of inaccuracy of the gas analysis.

As can be seem from the data of Table 3, activity of fresh catalyst is low. During the first hour and a half, it increases, and then remains constant, decreasing slowly afterward. From the products of propylene oxidation, only traces of aldehydes (0.1-0.2 vol. %) are found, even under optimal conditions, and likewise for acids (0.01-0.02%), with large amounts of CO_2 (2%) and CO (1.2-2%). This corresponds to a ratio of useful to useless products of 1:6 with fresh catalyst, and after one hour of work, to an average of 1:19.

It was not possible to increase the yield of useful compounds by modification of experimental conditions. A comparison of these data with the data of Table 1 indicates that this result cannot be limited by homogeneous oxidation, or by thermal decomposition of the reaction products.

In order to ascertain whether or not the low yields of aldehydes and of acids are the result of low formation rates for these substances, or their rapid oxidation on the catalyst, experiments were set up with formaldehyde, acetaldehyde and acetic acid.

Experiments with formaldehyde, using various mixture compositions, are given in Table 4.

TABLE 4

Oxidation of Formaldehyde on Vanadium Catalyst (V_2O_5) at 400°

Experimental conditions		Initial mixture (vol. %)		Reaction products (vol. %)					Yield of products (mol.%)*			% conversion of HCOH
flow rate (liters/hr)	contact time (sec.)	HCOH	O_2	acids	aldehydes	CO_2	CO	O_2	acids	CO_2	CO	
29	1.2	2.0	1.6	0.04	0.25	1.2	0.8	0	2.3	68.5	45.6	87
31	1.1	2.1	1.6	0.03	0.27	1.0	0.8	0	1.6	54.6	43.6	87
35	1.0	2.2	21.0	0.03	0.05	1.4	0.8	16.4	1.4	65	37.3	98

As can be seen from the data of Table 4, formaldehyde is about 87-98% converted at 400° and for a contact time of about 1 second; traces of acids (0.03 vol. %) were found in the reaction products, a small residue of non-oxidized formaldehyde (0.05-0.27 vol. %), and large amounts of CO_2 and CO. Thus, formaldehyde on vanadium catalyst is not stable in the presence of oxygen. The experiment with acetaldehyde carried out under the same conditions on vanadium catalyst gave the same results.

Experiments with acetic acid gave even higher percent conversion. The results obtained here are given in Table 5.

TABLE 5

Oxidation of Acetic Acid on Vanadium Catalyst (V_2O_5) at 400°, flow rate being 29 l./hr., contact time, 1.2 seconds

Initial mixture (in vol. %)		Reaction products (in vol. %)				Percent conversion
CH_3COOH	O_2	CH_3COOH	CO_2	CO	O_2	
2.0	0.4	0.06	2.2	0.02	0	97
2.1	1.6	0.05	1.8	0.02	0	98
2.3	1.6	0.07	2.6	0.02	0	97
2.0	21.0	0.06	2.2	1.2	17.6	97

As with aldehydes, acetic acid is unstable over vanadium catalyst in the presence of oxygen, and is 97-98% converted to carbon dioxide and carbon monoxide. The carbon balance forces us to assume that with insufficient oxygen (first three experiments) there is evidently also formed methane, determination of which was not carried out.

DISCUSSION OF RESULTS

Investigations of the authors have indicated the existence of qualitative differences in oxidation of propylene on silver and on vanadium oxide preparations studied. Reaction on silver begins at a considerably lower temperature, and proceeds almost to completion, with conversion of all three carbon atoms of each propylene molecule to carbon dioxide. From the products of incomplete oxidation, propylene oxide is found only in traces. Qualitative tests for aldehydes and carboxylic acids were negative. Taking into account the sensitivities of the analytical methods, and the approximate propylene oxide content and upper limits of concentrations of aldehydes and acids, evaluation of the reaction products, expressed in volume percent, gave: propylene oxide about 0.1, aldehydes less than 0.001, carboxylic acids less than 0.001.

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* Relative to theoretical yield calculated on the basis of reacted formaldehyde. The sum of reaction products is not equal to 100% due to inaccuracy of the gas analysis.

It is not clear whether the presence of traces of propylene oxide is due to slowness in its formation process from propylene, or whether propylene oxide forms with equal ease from propylene as ethylene oxide is formed from ethylene, but unlike the latter is too rapidly oxidized to carbon dioxide.

Upon oxidizing propylene on vanadium catalyst, the mole yield with respect to theory constitutes from 41.7 to 66.6% for carbon dioxide, and from 22.2 to 55.5% for carbon monoxide, calculating on the basis of propylene oxidized. A comparison of these data with the mole yield of carbon dioxide and carbon monoxide by oxidation of formaldehyde and acetic acid (Tables 4 and 5) makes it possible to assume that carbon dioxide and carbon monoxide are secondary products, formed principally because of oxidation of intermediate, readily oxidizable products.

Taking into account the high percentage conversion of aldehydes and acids on vanadium catalyst, it can be considered that the small concentrations of aldehydes and acids among the propylene oxidation products observed in the experiments can represent final concentrations of these substances formed by oxidation.

Comparisons of the carbon dioxide to carbon monoxide ratio, formed by oxidation of oxygen-containing organic compounds and propylene, makes possible an orientative evaluation of the possibility for direct propylene oxidation to final products, and subsequent oxidation through a stage of formation of intermediate products, in the vein of the Twigg [3, 4] scheme, which has been proposed by him for ethylene oxidation.

It appears possible that oxidation of propylene on vanadium under the authors' conditions proceeds mainly via the formation of unstable intermediates, which can be further oxidized at a high rate to carbon dioxide and carbon monoxide.

The ease of oxidation of aldehydes and acids may be the cause of low yields for readily-oxidizable products. The ratio of oxidation rates on vanadium catalyst for propylene used on the one hand by the authors, and that of formaldehyde, acetaldehyde and acetic acid on the other, excludes the possibility of attaining high yields of intermediate products. Yields, on hydrocarbon oxidized, can be increased by decrease in contact time, but the volume percentages are then decreased even more. In varying external conditions, the authors failed to change the unfavorable ratio of oxidation rates. This situation appears, as the authors see it, to be one of the possible causes for lack of success by other authors in their attempts to obtain aldehydes and carboxylic acids in adequate amounts by oxidation of unsaturated gases on vanadium catalyst. In order to obtain positive results, catalysts possessing considerably different ratios between oxidation rates of hydrocarbons and oxygen-containing compounds are necessary.

SUMMARY

1. Oxidation of propylene by oxygen of the air on silver catalyst proceeds almost to completion with conversion of all three carbon atoms of propylene to carbon dioxide.

2. Oxidation of propylene over vanadium pentoxide catalyst is accompanied by formation of carbon dioxide and carbon monoxide in considerable amounts and small amounts of aldehydes and carboxylic acids.

3. For the catalysts studied, there occurs an unfavorable ratio of rates of propylene oxidation on the one hand for accumulation of readily-formed oxidation products, and aldehydes and acetic acid on the other.

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BROMINATION OF UNSATURATED COMPOUNDS

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Results of work on bromination of unsaturated compounds by means of complexly-bound bromine are given in the present work. Dioxan dibromide and pyridine dibromide were used as brominating agents. The first complex, described for the first time by Favorsky [1], was proposed by Yanovskaya [2] for the bromination of polyhydroxy phenols, aldehydes and ketones, and other readily-converting compounds. Dioxan dibromide was utilized by Terentyev, Kostov, Yurkevich and Khaskina [3] for bromination of vinyl acetate, whereby the 1,2-dibromoester of acetic acid resulted in 50% yield. Pyridine bfomide was used [4] for addition of bromine at the double bond of safrole, p-methoxy-ω-nitrostyrene, and 3,4-methylenedihydroxy-ω-nitrostyrene, which forms only polybromides, with halogen in the ring, upon bromination in the usual manner with bromine in solvent.

The authors used dioxan dibromide for bromination of styrene, hexadiene-2,4, isoprene, acrolein, acrylonitrile, methacrylic acid and vinyl acetate, and in addition, bromination of styrene, isoprene and methacrylic acid by pyridine dibromide.

Reaction, as a rule, was carried out without solvent, and with gentle cooling of the reaction mixture with water. Addition took place in all cases. It was established in experiments with styrene that vinyl substitution (in the side chain) proceeds negligibly. Somewhat lower yields of bromination products are obtained with pyridine dibromide than with dioxan dibromide. Isolation and purification of final substances are extremely simple: the reaction mixture is treated with water and then extracted with ether. After drying the ether layer, the bromoderivative is separated by fractionation.

Thus, dioxan dibromide is found to be a convenient reagent for addition of bromine to various unsaturated compounds.

EXPERIMENTAL*

Bromination of styrene. 25 g (0.1 mole) of dioxan dibromide was added in portions to 10.4 g (0.1 mole) of styrene. Instantaneous decoloration was observed, and moderate heat evolution. The dibromide was precipitated with water, separated, washed well and dried in air. Yield of dibromide was quantitative – 26.4 g; m.p. was 73-74° (from dilute alcohol). A sample mixed with sample of dibromostyrene did not show depression in melting temperature.

Bromination of styrene with pyridine bromide. 2.6 g (0.025 mole) of styrene was added in small portions, with cooling and stirring, to 6 g (0.025 mole) of pyridine bromide dissolved in 20 ml of dichloroethane. Upon addition of the last portion of styrene, the red pyridine dibromide became decolorized. 25 ml of water was then added and titrated with 0.1 N NaOH solution in the presence of methyl orange. 40 ml of alkali was used for the titration. The resulting crystals were washed with water and dried m.p. was 73°. The yield of dibromostyrene was 4.7 g (about 70%). Recalculation of the alkali used for titration of the HBr indicated that the substitution reaction used 7.8% of the bromine in pyridine dibromide.

Bromination of hexadiene-2,4 with dioxan dibromide. 25 g (0.1 mole) of dioxan dibromide (with stirring and ice-cooling) was added in small portions to 11.8 ml (0.1 mole) of hexadiene-2,4 (b.p. 80-81°; n_D^{20} 1.4385; d_4^{20} 0.711), placed in a flask with ground stopper. The reaction mixture was treated and washed with ice water, after which it was extracted with ether. The ether extract was dried with calcium chloride, and after distilling off the ether, the substance was redistilled in vacuo. The main part distilled at 86-88° (11 mm). Yield was 15.2 g (86% of theory), calculating on the basis of dibromohexane; a yellow-brown oil with sharp odor and lachrymatory action, decolorizing bromine water and potassium permanganate, had d_4^{20} 1.632 and n_D^{20} 1.5335, which is in full agreement with the literature data for 2,5-dibromohexene-3, [5].

0.1956 g sub.: 0.3025 g AgBr. Found %: Br 65.82; M (cryoscopically in benzene) 240.35. $C_6H_{10}Br_2$. Calculated %: Br 66.05; M 241.97.

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* The experimental part was carried out with the participation of R. I. Abramovich.

Bromination of isoprene. 2.5 g (0.037 mole) of isoprene (b.p. 34°, d_4^{20} 0.6805, n_D^{20} 1.4215) was brominated with 17.6 g (0.073 mole) of dioxan dibromide. A heavy, yellow-brown oil resulting from treatment of the reaction mixture was obtained. After distillation in vacuo 12.7 g (89.3%) of colorless liquid resulted, with b.p. 32-32.5° (6 mm), d_4^{20} 1.548, n_D^{20} 1.5070.

0.1842 g sub.: 0.3566 g AgBr. Found %: Br 82.35; M (cryoscopically in benzene) 383.15. $C_5H_8Br_4$. Calculated %: Br 82.43; M 387.78.

30.6 g (76.3%) of the tetrabromide was obtained from 7.3 g (0.073 mole) of isoprene and 35.1 g (0.146 mole) of pyridine dibromide, possessing the same physico-chemical and analytical data.

Bromination of acrolein with dioxan dibromide. 7.1 ml (0.107 mole) of freshly distilled acrolein (b.p. 52°) was brominated, with continuous cooling and stirring, by 26.6 g (0.107 mole) of dioxan dibromide. The reaction mixture was treated with ice water and extracted with ether. The ether extract was dried with calcium chloride. After distilling off the ether, the residue was fractionated in vacuo. 16.7 g (72%) of colorless oil with sharp odor and lachrymatory properties, and a b.p. of 79-80° (14 mm) d_4^{20} 2.192, n_D^{20} 1.5082, these constants corresponding to the literature data for dibromopropionic aldehyde [6]. The dibromide did not decolorize bromine water or potassium permanganate. Addition of 2-3 drops of the substance to fuchsin—sulfuric acid solution caused appearance of an intense red-violet color, which indicated presence of the aldehyde group.

0.1928 g sub.: 0.3344 g AgBr. Found %: Br 73.83 M 212.62. $C_3H_4OBr_2$. Calculated %: Br 74.03; M 215.89.

Bromination of acrylonitrile. 10 ml (about 0.15 mole) of acrylonitrile (b.p. 73°, n_D^{20} 1.3914) was brominated at room temperature with 37 g (0.15 mole) of dioxan dibromide. Complete decolorization of the reaction mixture resulted after 24 hours. After washing with cold water, 30.5 g (about 95%) of a thick, oily substance was obtained which, after drying with calcium chloride, had a b.p. of 173° and n_D^{20} 1.5580; possessing lacrymatory action.

0.2008 g sub.: 0.3516 g AgBr. Found %: Br 74.51; N (according to Kjeldahl) 7.00; M (according to Rast) 209.6. $C_3H_3NBr_2$. Calculated %: Br 75.07; N 6.58; M 212.89.

Bromination of methacrylic acid. 9.8 ml (about 0.12 mole) of methacrylic acid (m.p. 15-16°, n_D^{20} 1.4312) was brominated at room temperature with 28.8 g (0.12 mole) of dioxan dibromide. Reaction was terminated after 3 hours. At the end of the reaction, the mixture separated into two layers. After treatment with ice water, the heavy oil was extracted with ether. The ether solution was dried with calcium chloride. Having distilled off the ether, the yellow-brown oil was heated again to 103-104° and then transferred to a vacuum desiccator. Colorless crystals separated after 12-15 days, which were pressed out on a porous plate and dried between sheets of filter paper. Yield was about 25.5 g (89% of theory, calculating on the basis of α,β-dibromomethacrylic acid). The crystals which were recrystallized from ether melted at 47°, corresponding to the literature data for α,β-dibromomethacrylic acid [7]. Solutions of the compound did not show reactions for the double bond.

0.1608 g sub.: 0.2451 g AgBr. Found %: Br 64.89; M 247.36. $C_4H_6O_2Br_2$. Calculated %: Br 65.02; M 245.92.

The equivalent amount of 10% potassium hydroxide solution was added to a hot aqueous solution of the dibromo acid. The solution was evaporated to dryness on a water bath, and the resulting potassium salt of 1-methyl-1,2-dibromopropionic acid was dried in a vacuum desiccator.

0.3264 g sub.: 0.1385 g KBr. Found %: K 13.94. $C_4H_5O_2Br_2K$. Calculated %: K 13.77.

4.9 g (0.058 mole) of methacrylic acid was brominated under analogous conditions with 13.8 g (0.058 mole) of pyridine dibromide. After appropriate treatment, 10.9 g (76.7%) of dibromo acid with m.p. 47° was isolated. A sample mixed with the compound synthesized earlier (with dioxan dibromide) did not show depression in melting temperature.

Bromination of methacrylate. 10.5 ml (0.116 mole) of methyl methacrylate (b.p. 80.5°, d_4^{20} 0.950, n_D^{20} 1.3983) was brominated by addition of 28.8 g (0.116 mole) of dioxan dibromide in small portions. The reaction mixture was left overnight until the following day, when it was washed with cold water and treated with ether; the ether extract was dried with calcium chloride. After distilling off the ether, the residue was kept in a vacuum desiccator and then fractionated in vacuo. 27.5 g (95% calculating on the basis of dibromide of methyl propionate) of colorless oil: b.p. 32° (4 mm), d_4^{20} 1.931, n_D^{20} 1.5122. The compound showed no reactions for double bond.

0.2014 g sub.: 0.3073 g AgBr. Found %: Br 64.98; M 247.27. $C_4H_6O_2Br_2$. Calculated %: Br 65.02; M 245.92.

Bromination of vinyl acetate. 10.7 ml (0.116 mole) of vinyl acetate (b.p. 73°, n_D^{20} 1.3958) was brominated with 28.8 g (0.116 mole) of dioxan dibromide, with stirring and cooling, with strong heat evolution and rapid decolorization. The brown reaction mixture was poured into ice water, the heavy oil washed several times with water, dried with calcium chloride, and distilled in vacuo. 22.5 g (78%) of colorless, gradually-yellowing oil was obtained with b.p. 70-72.5° (2 mm), d_4^{20} 1.918, n_D^{20} 1.5052. Possessing a lachrymatory action. Did not decolorize potassium permanganate or bromine water.

0.1734 g sub.: 0.2637 g AgBr. Found %: Br 64.73 M 241.44. $C_4H_6O_2Br_2$. Calculated %: Br 65.02; M 245.92.

SUMMARY

A new method for bromination of an unsaturated compound with dioxan dibromide has been proposed.

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* See Consultants Bureau Translation, page 1635.

** See Consultants Bureau Translation, page 1639.

*** See Consultants Bureau Translation, page 779.

neutralization. The above reaction mixture was poured into ice water, [illegible] washed with [illegible] and [illegible] obtained with m.p. [illegible] potassium permanganate or bromine water.

[illegible]

SUMMARY

A new method for [illegible] has been proposed.

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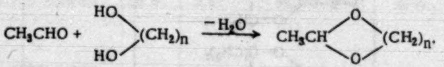
A METHOD FOR SYNTHESIS OF CYCLIC ACETALDEHYDEACETALS

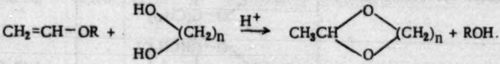
M. G. Voronkov and E. S. Titlinova

Up to the present time, the principal method for synthesis of cyclic acetaldehydeacetals (2-methyl-1,3-dioxacycloalkanes) has been the condensation of acetaldehyde with glycols [1-6], according to the scheme:

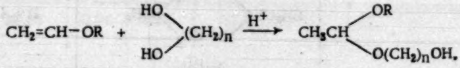


These compounds have also been obtained by reacting acetylene with glycols in the presence of mercury catalysts [7-10], and by transesterification of acetaldehydeacetals [11, 12].

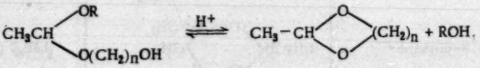
In 1948, the authors proposed a synthetic method for acetaldehydeacetals from vinyl ethylate and alcohols [13]. In the present work, the indicated reaction has been used for the synthesis of cyclic acetaldehydeacetals through the interaction of vinylalkyl esters with glycol, proceeding according to the general scheme:



Reaction proceeds through the stage of formation of mixed acetal



which, under the conditions of synthesis, is intramolecularly esterified



This intramolecular transesterification is readily shifted to the right by distillation of the resulting acetal from the reaction mixture, if it has a lower boiling point than the alcohol forming, or in the contrary case, by distilling off the alcohol which splits out. Thus, it is possible to obtain easily and smoothly cyclic acetaldehyde-acetals by interacting the corresponding glycols with vinyl esters of these alcohols, which have a boiling point sufficiently different from the boiling point of the forming acetal, in order that they may be capable of separation by distillation. For this purpose, a sufficiently practical application can be made only for the two most accessible vinylalkyl esters — vinylethyl ester and vinylbutyl ester.

Synthesis of cyclic acetals by the proposed method is realized by simple distillation on a column of the corresponding vinylalkyl ester and glycol mixture in the presence of 1-3 drops of concentrated HCl. Reaction proceeds with both α- and β-, as well as γ-glycols. By this procedure, the authors obtained two acetals with a seven-membered ring. The yields of cyclic acetaldehydeacetals amounted to 60-90% of theory, calculating on the basis of initial vinylalkyl ester. The acetals obtained, their physical constants, and analytical data are given in Table 1.

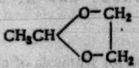
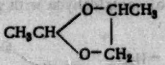
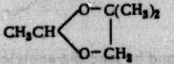
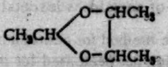
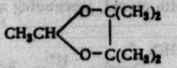
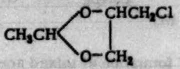
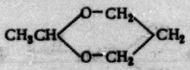
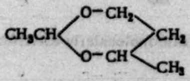
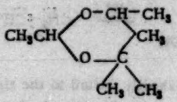
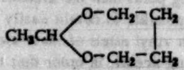
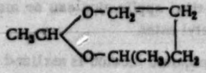
Analysis of the cyclic acetals was carried out according to the method of hydrolytic oximation [14]. Determinations were carried out in sealed tubes which were heated on a water bath for 3-10 hours.

EXPERIMENTAL

The vinylethyl ester and vinylbutyl ester were purified by the method described earlier [15]. All of the initial glycols were purified by distillation on a column with 15 theoretical plates effectiveness. Their physical constants and analytical data are given in Table 2.

TABLE 1

Cyclic Acetaldehydeacetals

Acetal	Formula	Boiling point under pressure (mm)	d_4^{20}	n_D^{20}
2-Methyl-1,3-dioxolane		82.3° (749)	0.9804	1.39705
2,4-Dimethyl-1,3-dioxolane		93.0 (755)	0.9283	1.3949
2,4,4-Trimethyl-1,3-dioxolane*		100.1 (762)	0.8916	1.3938
2,4,5-Trimethyl-1,3-dioxolane		108.5 (752)	0.9117	1.3998
2,4,4,5,5-Pentamethyl-1,3-dioxolane		134.8 (758)	0.8997	1.4121
2-Methyl-4-chloromethyl-1,3-dioxolane		148.5 (765)	1.1531	1.4397
2-Methyl-1,3-dioxane		110.4 (756)	0.9701	1.41394**
2,4-Dimethyl-1,3-dioxane		118.2 (740)	0.9354	1.4140
2,4,4,6-Tetramethyl-1,3-dioxane*		140.0 (766)	0.9039	1.4202
2-Methyl-1,3-dioxephane		127.5 (757)	0.9631	1.4260
2,4-Dimethyl-1,3-dioxephane*		138.0 (762)	0.9319	1.4233

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* Synthesized for the first time.

** n_C^{20} 1.41194 n_F^{20} 1.41878.

*** Crude product.

TABLE 1 (Continued)

$n_F^{20} - n_C^{20}$	MR_D found	MR_D calculated	Analysis calculated % C	Analysis calculated % H	Analysis found % C	Analysis found % H	Acetal content according to analysis (in %) ± 0.9%	Yield (in %)***
0.00668	21.64	21.76	54.53	9.15	54.42, 54.64	9.23, 9.32	99.8	87
0.0067	26.37	26.38	58.80	9.87	58.85, 58.73	9.90, 9.95	99.5	60
0.0066	31.15	30.99	62.04	10.41	62.26, 62.00	10.44, 10.49	99.0	70
0.0068	30.87	30.99	62.04	10.41	62.15, 62.19	10.40, 10.45	99.2	65
0.0070	39.89	40.23	66.63	11.18	66.25, 66.32	11.13, 11.18	99.6	60
0.0075	31.20	31.24	43.97	6.64	—	—	99.2	65
0.00684	26.30	26.38	58.80	9.87	58.60, 59.03	9.90, 9.65	99.8	92
0.0069	31.03	30.99	62.04	10.41	61.97, 61.80	10.38, 10.43	99.4	66
0.0070	40.39	40.23	66.63	11.18	66.49, 36.37	11.01, 11.11	99.6	71
0.0072	30.90	30.99	62.04	10.41	62.30, 62.37	10.39, 10.48	99.4	65
0.0071	35.60	35.61	64.58	10.84	64.42, 64.50	10.80, 10.75	99.4	70

Since the procedures for all of the syntheses were standard, the authors, therefore, have limited themselves to quotation of but a few experiments.

Synthesis of 2-methyl-1,3-dioxolane. (2-Methyl-1,3-dioxacyclopentane). 124 g (2 moles) of ethylene glycol, 180 g (1.8 moles) of vinylbutyl ester and several drops of hydrochloric acid were placed in a distilling flask and distillation column with 15 plates theoretical effectiveness.*

The reaction mixture was heated to boiling with complete return on the column in 30 minutes, after which it was distilled. Yield of 2-methyl-1,3-dioxolane with b.p. 81.5-82.5° was 138.2 g (87% of theory, calculating on the basis of initial vinylbutyl ester). Along with this, there was formed 131 g of butyl alcohol with b.p. 117.0-117.1°.

After a second distillation on the column, the 2-methyl-1,3-dioxolane had the constants given in Table 1.

TABLE 2

Physical Properties of the Initial Glycols

Formula	Boiling point under pressure (in mm)		d_4^{20}	n_D^{20}
$HOCH_2CH_2OH$	197.4	(760)	1.1132	1.4318
$HOCH_2CH_2CH_2OH$	214.5	(737)	1.0539	1.4390
$CH_3CH(OH)CH_2OH$	188.0	(768)	1.0379	1.4325
$HOCH_2CH_2CH_2CH_2OH$	228.0	(763)	1.0190	1.4458
$CH_3CH(OH)CH_2CH_2OH$	207.4	(759)	1.0049	1.4399
$CH_3CH_2CH(OH)CH_2OH$	190.9	(766)	1.0026	1.4379
$CH_3CH(OH)CH(OH)CH_3$	182.0	(758)	0.9870 (25°)	1.4307 (25°)
$(CH_3)_2C(OH)CH_2OH$	175.8	(748)	0.9967	1.4360
$CH_3CH(OH)CH_2CH_2CH_2OH$	221.5	(757)	0.9885	1.4470
$(CH_3)_2C(OH)C(OH)(CH_3)_2$	173.0	(762)	–	1.4326 (45°)
$(CH_3)_2C(OH)CH_2CH(OH)CH_3$	194.2	(752)	0.9239	1.4284
$ClCH_2CH(OH)CH_2OH$	113.0	(10)	1.3226	1.4797

Synthesis of 2-methyl-1,3-dioxane (2-methyl-1,3-dioxacyclohexane). 2 drops of concentrated HCl was added to a mixture of 36.1 g (0.5 mole) of vinylethyl ester and 61 g (0.8 mole) of trimethyleneglycol. The mixture was boiled for 15 minutes and distilled on a column. 24.0 g of ethyl alcohol with b.p. 78.5-78.6° and 47.0 g of 2-methyl-1,3-dioxane with b.p. 105.0-109.2° was obtained. The yield was 92% of theory. After treating with sodium in the cold, and distilling on the column, the compound had the constants given in Table 1.

Synthesis of 2,4-dimethyl-1,3-dioxephane (2,4-dimethyl-1,3-dioxacycloheptane). 3 drops of concentrated HCl was added to a mixture of 36.1 g (0.5 mole) of vinylethyl ester and 52 g (0.5 mole) of 1,4-pentandiol, and the mixture then distilled on the column. 20.2 g of ethyl alcohol of b.p. 77.0-78.9° and 45.6 g (70%) of 2,4-dimethyl-1,3-dioxephane with b.p. 135.5-138°. After a second distillation on the column, the compound had the constants given in Table 1.

All remaining acetals were synthesized by similar procedure from vinylethyl ester and the corresponding glycols.

SUMMARY

A method for synthesis of cyclic acetaldehydeacetals (2-methyl-1,3-dioxacycloalkanes) from vinylalkyl esters and glycols has been developed. According to this method, 11 acetaldehydeacetals with 5-, 6- and 7-membered rings (4 of them synthesized for the first time) have been obtained.

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* In all experiments, upon addition of the catalyst to vinyl ester and glycol, there were usually formed two immiscible layers and intensive exothermic reaction took place, which resulted in miscibility of the layers.

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* See Consultants Bureau Translation, page 255.

INVESTIGATIONS IN THE FIELD OF ALKANOSULFONIC ACIDS

XI. INTERACTION OF ALKANOSULFONYL CHLORIDES WITH p-CHLOROANILINE AND p-NITROANILINE

A. G. Kostsova

Reactions of alkanosulfonyl chlorides with aniline were described earlier by the author [1]. The present work had for its aim the problem of studying reactions of the above-mentioned sulfonyl chlorides with p-chloroaniline and p-nitroaniline. It was of interest in this respect to study the effect of the chlorine and of nitro group in a position para to the NH_2 group, upon the course of reaction and the properties of the resulting products.

The reaction with p-chloroaniline was carried out under the same conditions as with aniline, i.e., in ether medium with heating on a water bath. The experiments indicated that chlorine present in a position para to the NH_2 group does not affect markedly the course of the reaction, or the yields of p-chloroanilides, but does affect noticeably their physical properties, in particular, their melting temperatures, which, as a rule, increase sharply as compared with the corresponding unsubstituted anilides (see Table).

An exception to this general rule, to some degree, is the 2-methylethanesulfonyl-p-chloroanilide, whose melting point increases negligibly as compared with the anilide of the same sulfonic acid.

p-Chloroanilides and the unsubstituted anilides are white, crystalline compounds, readily soluble in alkalies, but their alkaline solutions are more difficult to methylate with methyl iodide as compared with the unsubstituted anilides. Thus, upon methylating p-chloroanilides prepared by the authors, the methyl derivatives of butan- and 2-methylbutan-p-chloroanilide, could be isolated in the form of crystalline powders, but their crystallization proceeded very slowly. The remaining p-chloroanilides became methylated only with great difficultly, even upon contact with methyl iodide for many days.

The products of methylation in this case resulted as oily traces on the surface of the alkaline solution, and to isolate, purify and characterize them, did not seem feasible. Methylation of alkansulfonyl-p-chloroanilides proceeds according to the general equation:

$$RSO_2NHC_6H_4Cl + CH_3I + NaOH \rightarrow RSO_2N(CH_3)C_6H_4Cl + NaI + H_2O.$$

Reaction of alkanosulfonyl chlorides with p-nitroaniline was carried out in pyridine medium while heating on a water bath. In this case, reaction proceeds very slowly. The reaction products — alkanosulfonyl-p-nitroanilides, are formed in negligible yield as a rule: 2-methylethane-, 2-methylpropane- and phenylmethanesulfonyl chloride do not react on the whole with p-nitroaniline under the conditions indicated.

Thus, with p-nitroaniline, the reaction course differs noticeably from that for unsubstituted aniline. The alkanosulfonyl-p-nitroanilides formed, in contrast to p-nitroaniline itself, are in the form of colorless compounds, but when dissolved in alkali, in which they are poorly soluble, it should be mentioned that the anilides and p-chloroanilides produce yellow solutions, while, when dissolved in boiling water, they produce colorless solutions, which prompts one to make the assumption that their sodium salts are colored.

Alkanosulfonyl-p-nitroanilides, in distinction to other N-arylamides described in the authors [1], are poorly soluble in alcohol. Alcoholic solutions, like N-arylamides, are readily precipitated by water.

The reaction of methanesulfonyl chloride with m-nitroaniline was also studied by the authors. There were no profound differences in reaction with p-nitroaniline for the given case. The reaction product was formed in small amount as colorless crystals; its alkaline solutions are also yellow in color, and the aqueous solutions colorless.

The melting points of alkanosulfonyl-p-nitroanilides are, as a rule, higher than for alkanosulfonyl-p-chloroanilides, and the melting points of the latter are higher than for unsubstituted alkanosulfonylanilides (see Table).

TABLE

Melting Points of Anilides: The p-Chloro- and p-Nitroanilides of Alkanosulfonyl Acids

Alkanosulfonylanilides	M.p.	Alkanosulfonyl-p-chloroanilides	M.p.	Alkanosulfonyl-p-nitroanilides	M.p.
$CH_3SO_2NHC_6H_5$	99°	$CH_3SO_2NHC_6H_4Cl$	148°	$CH_3SO_2NHC_6H_4NO_2$	183°
$C_2H_5SO_2NHC_6H_5$	55	$C_2H_5SO_2NHC_6H_4Cl$	121	$C_2H_5SO_2NHC_6H_4NO_2$	162
iso-$C_3H_7SO_2NHC_6H_5$	84	iso-$C_3H_7SO_2NHC_6H_4Cl$	87	—	—
n-$C_4H_9SO_2NHC_6H_5$	35	n-$C_4H_9SO_2NHC_6H_4Cl$	62	n-$C_4H_9SO_2NHC_6H_4NO_2$	91
iso-$C_5H_{11}SO_2NHC_6H_5$	42	iso-$C_5H_{11}SO_2NHC_6H_4Cl$	61	iso-$C_5H_{11}SO_2NHC_6H_4NO_2$	112

EXPERIMENTAL *

p-Chloroaniline, with m.p. 70-71°, chemically-pure, was used for the reaction. p-Nitroaniline had a m.p. of 146-147°. All alkanosulfonyl-p-chloroanilides were obtained according to the same procedure and, therefore, a detailed account is given only for the first representative.

A description and the procedure for alkanosulfonyl-p-nitroanilide are also given.

1. Synthesis of methanesulfonyl-p-chloroanilide. 2 g of methanesulfonyl chloride in 30 ml of anhydrous ether and 4.4 g of p-chloroaniline were heated on a water bath at 40-45° under reflux for 1.5-2 hours. After termination of heating, the reaction mixture was left to the following day; the p-chloroaniline hydrochloride which resulted from the reaction was separated, the ether filtrate evaporated or distilled off on a water bath. The solid yellow precipitate was treated with 5% alkali. The portion which did not dissolve was separated, and the alkaline solution was acidified with dilute hydrochloric acid to a stable turbidity, from which, when cooled with ice, and rubbing with a glass rod, fine white crystals of methanesulfonyl-p-chloroanilide precipitated. The precipitate was isolated and dried. The yield was 2 g (55.5%). Recrystallized from alcohol and water; soluble in organic solvents (alcohol, ether, acetone and others), poorly soluble in water.

0.1012 g sub.: 4.95 ml 0.1 N H_2SO_4. 0.095 g sub.: 0.1090 g $BaSO_4$. Found %: N 6.84; S 15.73.
$C_7H_8O_2NSCl$. Calculated %: N 6.82; S 15.60.

2. Synthesis of ethanesulfonyl-p-chloroanilide. 1 g of ethanesulfonylchloride, 1.98 g of p-chloroaniline and 20 ml of anhydrous ether were taken. The yield of ethanesulfonyl-p-chloroanilide was 1.24 g (73%). Recrystallized from alcohol and water. White, fine, fluffy crystals.

0.1182 g sub.: 5.29 ml 0.1 N H_2SO_4. 0.1328 g sub.: 0.1384 g $BaSO_4$. Found %: N 6.26; S 14.29.
$C_8H_{10}O_2NSCl$. Calculated %: N 6.30; S 14.50.

3. Synthesis of 2-methylethanesulfonyl-p-chloroanilide. 2 g of 2-methylethanesulfonyl chloride, and 4 g of p-chloroaniline, in 30 ml of anhydrous ether were taken. The yield of 3-methylethanesulfonyl-p-chloroanilide was 1.3 g (40.6%).

0.1284 g sub.: 0.24 ml 0.1 N H_2SO_4. 0.1512 g sub.: 0.1514 g $BaSO_4$. Found %: N 5.71; S 13.72.
$C_9H_{12}O_2NSCl$. Calculated %: N 5.99; S 13.70.

4. Synthesis of butanesulfonyl-p-chloroanilide. 1 g of butane sulfonyl chloride, and 1.73 g of p-chloroaniline, in 20 ml of anhydrous ether, were taken. The yield of butanesulfonyl-p-chloroanilide was 1 g (56.8%). Slightly yellowish, fine crystals.

0.0991 g sub.: 3.98 ml 0.1 N H_2SO_4. 0.1420 g sub.: 0.1330 g $BaSO_4$. Found %: N 5.62; S 12.84.
$C_{10}H_{14}O_2NSCl$. Calculated %: N 5.65; S 12.92.

5. Synthesis of 2-methylbutanesulfonyl-p-chloroanilide. 1 g of 2-methylbutanesulfonyl chloride and 1.5 g of p-chloroaniline, in 20 ml of anhydrous ether, were taken. The yield of 2-methylbutanesulfonyl-p-chloroanilide was 0.77 g (50.3%).

0.0350 g sub.: 1.22 ml 0.1 N H_2SO_4. 0.0740 g sub.: 0.0670 g $BaSO_4$. Found %: N 4.88; S 12.41.
$C_{11}H_{16}O_2NSCl$. Calculated %: N 5.35; S 12.23.

6. Methylation of butanesulfonyl-p-chloroanilide. 0.2 g of butanesulfonyl-p-chloroanilide was dissolved in a small amount of 7 % caustic alkali (the alkali being added dropwise to p-chloroaniline to dissolution). 0.6 g of methyl iodide (four-fold excess over the calculated) was added to the alkaline solution. The resulting emulsion

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* L. D. Yakimova and V. D. Levitan participated in the experimental work.

was heated on a round-bottomed flask with reflux condenser, on a water bath at 45-50° for 40-45 minutes. The flask with reaction mixture was then left standing for 24 hours, and the flask contents then transferred to a Petri dish for evaporation of the excess methyl iodide. Oily spots remained on the surface of the alkaline solution, which upon prolonged rubbing with a glass rod, crystallized. The crystals were separated from the alkaline solution and washed with water on a filter. The yield was 1.8 g (90%). It was recrystallized from alcohol and water. The m.p. was 59°. Butanesulfonyl-N-methyl-p-chloroaniline is insoluble in alkali, and in water, readily soluble in alcohol, ether, benzene and acetone.

0.081 g sub.: 3.15 ml 0.1 N H_2SO_4. Found %: N 5.44. $C_{11}H_{16}O_2NSCl$. Calculated %: N 5.35.

7. Methylation of 2-methylbutanesulfonyl-p-chloroanilide. 0.2 g of 2-methylbutanesulfonyl-p-chloroanilide in 5 ml of 6% alkali and 0.44 g of methyl iodide were taken. Procedure was analogous to the preceeding. Yield was 0.17 g (81%). 2-Methylbutanesulfonyl-N-methyl-p-chloroanilide: colorless, fine crystals with m.p. 54-55°.

0.0436 g sub.: 1.56 ml 0.1 N H_2SO_4. Found %: N 5.00. $C_{12}H_{18}O_2NSCl$. Calculated %: N 5.08.

8. Synthesis of methylanesulfonyl-p-nitroanilide. 1.5 g of methanesulfonyl chloride was added to 1.8 g of p-nitroaniline which was dissolved in 10 ml of pyridine. Spontaneous evolution of heat from the reaction mixture at 20-25° was observed. To complete reaction, the mixture was heated on a water bath with reflux condenser at 60-70° for 1-1.5 hours, and then left to stand for 24 hours. The transparent, dark-brown pyridine solution was precipitated with cold water, and acidified with hydrochloric acid. An orange-red precipitate separated, representing a mixture of unreacted p-nitroaniline and the product of reaction, methanesulfonyl-p-nitroanilide. The latter was isolated when treated with alkali in which it dissolved while the p-nitroaniline did not dissolve. The methanesulfonyl-p-nitroanilide was precipitated from the alkaline extract with dilute sulfuric acid. Treatment with alkali was repeatedly carried out. The methanesulfonyl-p-nitroanilide precipitated out in the form of fine, fluffy, creamy crystals from the acidified solution. Their second dissolution in alkali and subsequent precipitation with acid, or recrystallization from alcohol and water, resulted in colorless crystals. The yield was 0.4 g (14.3%).

0.075 g sub.: 6.91 ml 0.1 N H_2SO_4. Found %: N 12.89. $C_7H_8O_4N_2S$. Calculated %: N 12.96.

9. Synthesis of ethanesulfonyl-p-nitroanilide. 1 g of ethanesulfonylchloride and 1 g of p-nitroaniline in 6 ml of pyridine were taken. Yield of ethanesulfonyl-p-nitroanilide was 0.2 g (11.1%). Fine, colorless, fluffy crystals.

0.053 g sub.: 4.58 ml 0.1 N H_2SO_4. Found %: N 12.09. $C_8H_{10}O_4N_2S$. Calculated %: N 12.18.

10. Synthesis of butanesulfonyl-p-nitroanilide. 1 g of butanesulfonyl chloride and 0.9 g of p-nitroaniline dissolved in 6 ml of pyridine were used. Yield of the butanesulfonyl-p-nitroanilide was 0.1 g (6%). The reaction product was at first a yellowish-pink and after two purifications by dissolution in alkali, and precipitation with acid, became completely colorless.

0.060 g sub.: 4.55 ml 0.1 N H_2SO_4. Found %: N 10.61. $C_{10}H_{14}O_4N_2S$. Calculated %: N 10.85.

11. Synthesis of 2-methylbutanesulfonyl-p-nitroanilide. 1.35 g of 2-methylbutanesulfonyl chloride and 1.1 g of p-nitroaniline in 7 ml of pyridine were used. The yield of 2-methylbutanesulfonyl-p-nitroanilide was 0.11 g (5%). 0.7 g, i.e., over 50% of the p-nitroaniline, which was taken for reaction and did not react, was isolated. The reaction product was recrystallized from alcohol and water.

0.068 g sub.: 4.91 ml 0.1 N H_2SO_4. Found %: N 10.10. $C_{11}H_{16}O_4N_2S$. Calculated %: N 10.29.

12. Synthesis of methanesulfonyl-m-nitroanilide. 1.5 g of methanesulfonyl chloride and 1.8 g of m-nitroaniline in 10 ml of pyridine were used for the reaction. The yield of methanesulfonyl-m-nitroanilide was 0.5 g (18%). Slightly-pink-yellow crystals, becoming almost colorless on recrystallizing from alcohol and water. M.p. 164°.

0.081 g sub.: 7.31 ml 0.1 N H_2SO_4. Found %: N 12.63. $C_7H_8O_4N_2S$. Calculated %: N 12.96.

SUMMARY

1. p-Chloroanilides, namely, methane-, ethane-, 2-methylane-, butane- and 2-methylbutanesulfonyl acids, have been synthesized and characterized.

2. It has been demonstrated that butane- and 2-methylbutanesulfonyl-p-chloroanilides are relatively easy to methylate, the lower homologs methylating with greater difficulty.

3. The p-nitroanilides of methane-, ethane, butane- and 2-methylbutanesulfonic acids, and the m-nitroanilide of methanesulfonic acid have been synthesized and characterized.

4. The effects of chlorine and nitro groups in the para position to the NH_2 group upon the reaction course, the melting point, and other properties of the compounds forming, have been demonstrated.

5. The conditions used by the authors for 2-methylethane-, 2-methylpropane- and phenylmethanesulfonyl chlorides, do not apply to p-nitroaniline.

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SPIRO-(2,4)-HEPTANE

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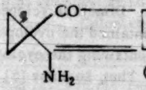
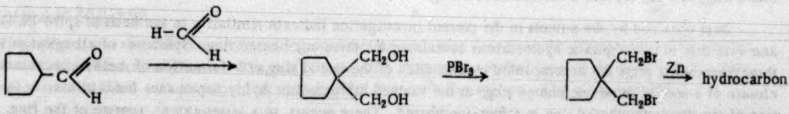
The first attempt to synthesize spiro-(2,4)-heptane was undertaken by Radulescu [1] in 1909 by condensation of the diethyl ester of cyclopropandicarboxylic acid with the diethyl ester of succinic acid, in the presence of sodium ethylate and sodamide. Resulting from the reaction was the formation of spirane (I),



(I)

which failed to convert into the hydrocarbon. There are no other indications in the literature of attempts to synthesize spiroheptane.

In the present investigation, the spiroheptane synthesis was carried out according to the scheme:



1,1-Dimethylolcyclopentane [2] was obtained by condensation of cyclopentylformaldehydewith formaldehyde in alkaline medium, which, upon reaction with PBr_3, was converted into the dibromide, and finally, by reacting the bromide with zinc dust, the hydrocarbon was obtained.

In the dispersion spectrum for the hydrocarbon, a line with frequency of 1650 cm^{-1} was found, a fact which indicates the presence of a hydrocarbon with double bond.

Fractionation of the hydrocarbon on a microcolumn with an effectiveness of 30 theoretical plates, gave two fractions: b.p. 98.6-99.6° and 105.6-106.6°. The low boiling fraction did not represent an individual compound: in its dispersion spectrum, the band at frequency 1650 cm^{-1} was weakened.

To determine the composition and structure of the resulting hydrocarbon mixture, it was ozonized. Upon decomposition of the ozonide with water, an oily layer floated to the top, which was found to be the hydrocarbon.

B.p. 98°; d_4^{20} 0.8203; n_D^{20} 1.43762; MR_D 30.69. C_7H_{12}; calculated 30.83 (increment for three-membered ring 0.7).

There was no maximum in the range 5.95-6.25 μ for the infra-red absorption spectrum of the hydrocarbon, which indicated the absence of a double bond. The manner of synthesis and the physical properties of the hydrocarbon made it possible to attribute to it the structure of spiro-(2,4)-heptane. For comparison, there are given in the table the properties for spiro-(2,4)-heptane and those of its nearest homolog, spiro-(2,5)-octane [3].

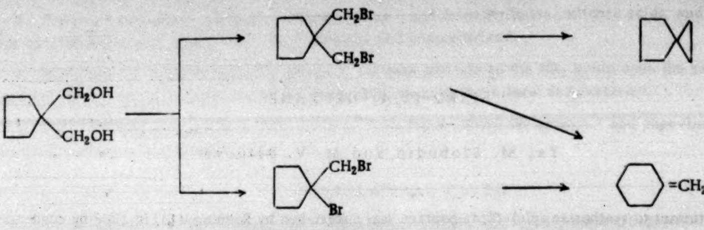
TABLE

Name of hydrocarbon	B.p.	d_4^{20}	n_D^{20}
Spiro-(2,4)-heptane	98°	0.8203	1.4376
Spiro-(2,5)-octane	125.5	0.8282	1.4476

Formic acid and cyclohexanone were found among the decomposition products of the ozonide, which could have been formed as the result of ozonolysis of methylenecyclohexane. For quantitative characterization of the hydrocarbon mixture in the boiling range of 98-101°, it was hydrogenated. The amount of hydrogen absorbed amounted to 48.9%, calculating on the basis of the hydrocarbon, C_7H_{12}, with one double bond. The bromine numbers indicated a somewhat higher degree of unsaturation, evidently related to the ease of rupture of the three-membered ring of spiroheptane.

Thus, from the synthesis, there resulted a hydrocarbon mixture consisting of spiroheptane and methylenecyclohexane.

Formation of methylenecyclohexane was found to be the result of a partial rearrangement, which can occur both during synthesis of the bromide from dimethylolcyclopentane, as well as during synthesis of the hydrocarbon by reaction with zinc bromide in the process of forming.



The expansion of a five-membered ring into a six-membered ring under the influence of chemical reagents has been observed many times. Thus, Nametkin and Morozova [4], by reacting hydrogen halide acids with cyclopentylcarbinol, obtained a mixture of bromomethylcyclopentane and cyclohexyl bromide. Dimethylcyclopentylcarbinol reacted with HBr and converted into a mixture of two bromides, one of which contained the cyclopentane ring, and the other the cyclohexane ring. By reacting dehydrating agents with alcohols containing the cyclopentyl radical, expansion of the five-membered ring into a six-membered ring also took place. Thus, Rozanov [5], by dehydrating cyclopentylcarbinol with oxalic acid, obtained cyclohexene. Nametkin and Gabriadze [6], by dehydrating dimethylcyclopentylcarbinol, observed the formation of two hydrocarbons, one of which contained a five-membered ring, and the second, a six-membered ring.

Data obtained by the authors in the present investigation indicate similarity in synthesis of spiro-(2,4)-heptane with that of other spirane hydrocarbons containing the three-membered ring. Syntheses of all spiranes with three-membered rings are accompanied by expansion of the initial ring,with formation of methylenecyclanes. Thus, closure of a second three-membered ring, in the strained dibromodimethylcyclopropane, leads primarily to expansion of the three-membered ring to a four-membered. There occurs, to a lesser extent, rupture of the ring, with formation of the unsaturated hydrocalbon containing an open chain of carbon atoms. Under the usual conditions, formation of spiropentane does not take place [7].

Closure of the three-membered ring in the less-strained dibromodimethylcyclobutane leads to exapnsion of the four-membered ring to a five-membered ring. Formation of an unsaturated hydrocarbon with an open chain of carbon atoms does not occur. Under normal conditions, spirohexane likewise does not form [8].

Finally, closure of the three-membered ring in unstrained dibromodimethylcyclopentane leads to expansion of the initial five-membered ring into a six-membered ring. At the same time, formation of considerable amounts of spiroheptane was observed.

EXPERIMENTAL

1,1-Dimethylolcyclopentane

Cyclopentylformaldehyde was the initial material used for synthesis of 1,1-dimethylolcyclopentane.

B.p. 40° (17 mm) d_4^{20} 0.9262; n_D^{20} 1.44145. Found %: C 73.32; H 10.24. Calculated %: C 73.47; H 10.20.

Semicarbazone: m.p. 135-137°. Found %: N 27.41. Calculated %: N 27.42.

On storage, the aldehyde polymerized partially. The polymer melted at 117°; M 330. Calculated: $(C_6H_{10}O)_3$ M 228; $(C_6H_{10}O)_4$. M 384.

Literature data for cyclopentylformaldehyde [9, 10]: b.p. 48° (21 mm), 52-53° (24 mm); semicarbazone: m.p. 125°; polymer: m.p. 117-117.5°.

Dispersion Spectrum of the Aldehyde

290 (1), 359 (1), 434 (5), 772 (1), 895 (10), 930 (1), 964 (3), 1012 (4), 1036 (1), 1081 (2), 1098 (3), 1153 (1), 1201 (1), 1300 (2), 1340 (1), 1393 (8), 1451 (10), 1481 (1), 1718 (10), 2868 (15), 2913 (5), 2961 (20 b. db.).

115 g of 30% formalin and 400 ml of water were placed in a flask equipped with stirrer and two dropping funnels, 57 g of cyclopentylformaldehyde was added from one dropping funnel, with vigorous stirring, and from the other was dispensed a suspension made of 26 g $Ca(OH)_2$ in 200 ml of water. Temperature was maintained at 30°. After addition of the reagents, the flask was heated to 50° and kept at this temperature for 1 hour. The mixture was cooled, and the excess $Ca(OH)_2$ filtered off. The filtrate was neutralized and concentrated in vacuo. The crystals which precipitated were filtered off. The diol was extracted with dichloroethane for 5-7 days. After

crystallization from dichloroethane, there was obtained 1,1-dimethylolcyclopentane in high purity. The yield was 86%.

B.p. 91-93°.

Found %: C 64.90; H 10.72. $C_7H_{14}O_2$. Calculated %: C 64.61; H 10.77.

1,1-Dibromodimethylcyclopentane

16.8 g of PBr_3 was placed in a flask, and with ice-water cooling, 10 g of the diol and 2 g of pyridine were introduced in small portions. The mixture was kept for 1 hour at room temperature, and was then heated on a boiling water bath to completion of HBr evolution. The reaction product was poured into cold water, extracted with ether, dried, and distilled. The yield was 40%.

B.p. 122-124° at 15 mm d_4^{20} 1.6644 n_D^{20} 1.5344. MR_D 47.84; calculated 47.85. Found %: Br 62.00. $C_7H_{12}Br_2$. Calculated %: Br 62.50.

Combined Dispersion Spectrum for the Dibromide

238 (4), 310 (1), 335 (1), 437 (4), 453 (2), 473 (1), 558 (2), 591 (3 b), 648 (10 b), 816 (1), 870 (1), 899 (1), 986 (2), 1005 (4), 1201 (2), 1253 (3), 1300 (2), 1351 (3), 1390 (2), 1430 (3), 1453 (6), 2872 (5 b), 2921 (3 b), 2965 (8 b), 3013 (3).

Spiro-(2,4)-heptane

The hydrocarbon was obtained by splitting out bromine with zinc dust from the dibromide in 85% alcohol. The bromide was added slowly from a dropping funnel. The mixture was boiled for 2 hours under reflux. The hydrocarbon was distilled with steam, dried, and distilled over metallic sodium. The yield was 90%.

B.p. 102-107°; d_4^{20} 0.8378; n_D^{20} 1.4510.

Combined Dispersion Spectrum for the Hydrocarbon

264 (2), 346 (1), 402 (3), 442 (3 b), 498 (5 b), 543 (1), 583 (1), 623 (2), 678 (1), 708 (3), 762 (4 b), 894 (3), 952 (10), 976 (2), 1025 (4 b), 1072 (1), 1106 (3), 1144 (2), 1181 (2), 1225 (3), 1271 (2), 1356 (6), 1439 (8), 1650 (5), 2860 (5), 2904 (2), 2936 (5), 2961 (5), 2992 (5).

In the second experiment, bromine was split out from the dibromide by means of zinc dust in the presence of sodium carbonate and sodium iodide. The hydrocarbon which resulted in this case hardly differed from the above-described hydrocarbon in its properties and spectrum.

The hydrocarbon was distilled on a microcolumn with an effectiveness of 30 theoretical plates, fractions with b.p. 98.5-99.5° (n_D^{20} 1.43994) and with b.p. 105.5-106.5° (n_D^{20} 1.45257), being isolated. The lower-boiling fraction was rich in spiroheptane. Spectroscopic investigation, however, indicated that it was not free from unsaturated hydrocarbons, although the frequency of the double bond was considerably weakened.

0.5054 g of hydrocarbon were hydrogenated over platinum catalyst. 60.8 ml (18.8°, 772 mm) or 48.9%, calculated on the basis of one double bond reduced.

The bromine number indicated content of unsaturated at 60%.

To determine the nature of the unsaturated hydrocarbon in the resulting mixture, the higher boiling fraction was ozonized. Ozonization was carried out in ethyl chloride. The ozonide was decomposed with water. An oily layer floated to the top, which was found to be the hydrocarbon. Its properties are given above.

After decomposition of the ozonide, alkali titration data indicated an acid content, calculated as formic acid, of 0.788 g. Determination of formic acid according to the calomel method indicated its content to be 0.740 g. Thus, the formic acid content in the ozonolysis products coincided quite well with the total acidity. The alkaline solution was extracted with ether. After removal of the ether, the residue was treated with 2,4-dinitrophenylhydrazine. After one recrystallization from alcohol, the 2,4-dinitrophenylhydrazone melted at 154-155°. A sample mixed with the 2,4-dinitrophenhylhydrazone prepared from pure cyclohexanone, melted without depression at 154-156°.

SUMMARY

1. 1,1-Dimethylolcyclopentane, in 86% yield, has resulted by condensation of cyclopentylformaldehyde with formaldehyde in alkaline medium.

2. Splitting out of bromine from 1,1-dibromodimethylcyclopentane by zinc dust leads to the formation of a hydrocarbon mixture which contains about 40% of spiro-(2,4)-heptane and about 60% methylenecyclohexane.

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* See Consultants Bureau Translation, page 2181.

** See Consultants Bureau Translation, page 37

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CYCLOHEXANONE DERIVATIVES OF MONOSES AND POLYHYDROXY ALCOHOLS

V. F. Kazimirova

Acetone derivatives of monoses and of polyhydroxy alcohols have been described in detail in the literature [1], and have been used for synthesis of other compounds. Cyclohexanone derivatives are encountered less frequently [2] and are less well-known. Dicyclohexylidene-d-xylose, dicyclohexylidene-l-arabinose, dicyclohexylidene-l-sorbose, as well as tricyclohexylidene-mannite, dicyclohexylidene-dulcite and cyclohexylidene-glycerine, described in the present article, were obtained by condensation of monoses and polyhydroxy alcohols with cyclohexanone, in the presence of sulfuric acid.

It is convenient to carry out the reaction in ether, benzene, or petroleum ether solution. Cyclohexanone and concentrated sulfuric acid were added to the monose or alcohol suspension in one of the enumerated solvents; the mixture was stirred, and the cyclohexanone compound which was in process of formation, went into solution, from which, after neutralization, it crystallized out. Crystallization took place quite readily at low temperature. The cyclohexanone compound crystallized well, melted above the corresponding acetone compounds, dissolved readily in ether, benzene, petroleum ether, acetone, alcohol, and other organic solvents, was insoluble in water and volatile with solvent vapors.

EXPERIMENTAL

Dicyclohexylidene-l-arabinose. 15 ml of cyclohexanone and 1.5 ml of concentrated sulfuric acid were added to a suspension of 7 g of pure, dry, l-arabinose in 40 ml of ether. The mixture was stirred for 8 hours, and then left for 24 hours. Practically everything dissolved after 2 hours, but if condensation was terminated at this stage, then the yield of dicyclohexylidene-arabinose was lower. The ether layer was separated from the oily layer and neutralized with dry sodium carbonate. After cooling, the solution crystallized. The crystals were separated from the residue by filtration, and purified by recrystallization from petroleum ether. The yield was 6.5 g (46%).

M.p. 73-74°; $[\alpha]^{20} -4.8°$ in benzene (c 2.159; l 0.9504).

0.1740 g sub.: 0.4190 g CO_2; 0.1317 g H_2O. 0.5320 g sub.: 18.21 g benzene: Δt 0.516°. Found %: C 65.67; H 8.45; M 307. $C_{17}H_{25}O_5$. Calculated %: C 66.80; H 8.38; M 310.

Dicyclohexylidene-d-xylose. Synthesis was carried out in a manner analogous to that for dicyclohexylidene-arabinose. 6.7 g (43%) of dicyclohexylidene-xylose was obtained from 7.5 g of d-xylose. Crystallized from petroleum ether; colorless needles, clustered into nodules; volatile with solvent vapors.

M.p. 102.5-103°; $[\alpha]^{21} +21.5°$ in benzene (c 2.44; l 0.9504).

0.1348 g sub.: 0.3258 g CO_2; 0.0997 g H_2O. 0.5126 g sub.: 16.80 g benzene: Δt 0.505°. Found %: C 65.91; H 8.28; M 309. $C_{17}H_{26}O_5$. Calculated %: C 65.80; H 8.38; M 310.

Dicyclohexylidene-l-sorbose. 20 ml of cyclohexanone and 3 ml of concentrated sulfuric acid were added to 9 g of pure, dry l-sorbose suspension in 60 ml of petroleum ether. The mixture was stirred for 12 hours and left for 24 hours. 30 ml of petroleum ether was added; neutralization with dry sodium carbonate; filtered. After cooling, a crystalline precipitate separated, which was removed, by filtration, from the yellow syrup and crystallized from petroleum ether. Yield was 5.6 g (42%); volatile with solvent vapors.

M.p. 118-119°; $[\alpha]^{20} -12.59°$ in benzene (c 2.506; l 0.9504).

15.10 mg sub.: 35.21 mg CO_2; 11.55 mg H_2O. 20.11 mg sub.: 46.98 mg CO_2; 15.34 mg H_2O. 0.4764 g sub.: 16.37 g benzene: Δt 0.44°. Found %: C 63.60, 63.71; H 8.50, 8.48; M 339. $C_{18}H_{28}O_6$. Calculated %: C 63.53; H 8.23; M 340.

Tricyclohexylidene-mannite. A mixture of 10 g of mannite, 50 ml of dry benzene, 30 ml of cyclohexanone and 3.5 ml of concentrated sulfuric acid was stirred for 8 hours and left overnight. The benzene solution was separated from a small oily layer, neutralized with dry sodium carbonate, and filtered. The solvent was evaporated at low temperature. After crystallization from petroleum ether, colorless crystals resulted. Yield was 10 g (58.7%).

M.p. 82-83° $[\alpha]^{20}$ −4.5° in benzene (c 2.55; l 0.9504).

0.1316 g sub.: 0.3301 g CO_2; 0.1072 g H_2O. 0.5208 g sub.: 17.23 g benzene: Δt 0.37°. Found %: C 68.42; H 9.13 M 420. $C_{24}H_{38}O_6$. Calculated %: C 68.24; H 9.05; M 422.

Tricyclohexylidene-mannite dissolves very readily in benzene at room temperature, and it is most convenient to carry out condensation of mannite with cyclohexanone in this solvent.

Dicyclohexylidene-dulcite. 10 g of dulcite, 20 ml of cyclohexanone and 3 ml of concentrated sulfuric acid were stirred for 8 hours and left for 24 hours. The solidified mass was washed thoroughly with water, dilute sodium carbonate solution, and water. Colorless crystals resulted, which were recrystallized from alcohol. The yield was 8.6 g (45%). Melting point of the dry compound was 137°.

14.00 mg sub.: 32.41 mg CO_2; 10.83 mg H_2O. 18.61 mg sub.: 43.00 mg CO_2; 14.76 mg H_2O. 0.22 g sub.: 24.50 g dioxan (K 48): Δt 0.13°. Found %: C 63.18, 63.06; H 8.66, 8.87; M 331. $C_{18}H_{30}O_6$. Calculated %: C 63.15; H 8.77; M 342.

Dicyclohexylidene-sorbite. A viscous oil.

Cyclohexylidene-glycerine. 27 g of pure, anhydrous glycerine, 60 ml of cyclohexanone, 4.5 ml of concentrated sulfuric acid and 75 ml of petroleum ether were stirred for 12 hours and left at room temperature for 48 hours. The ether solution was neutralized with dry sodium carbonate, and the solvent filtered by suction under reduced pressure. The reaction product was distilled two times, b.p. 118-120° at 5 mm. Yield was 22.3 g (44.6%), colorless liquid soluble in ether, benzene, chloroform, insoluble in water.

n_D^{21} 1.484 d_{20}^{20} 1.0961; d_4^{20} 1.0931.

0.1521 g sub.: 0.3517 g CO_2; 0.1280 g H_2O. Found %: C 63.05; H 9.40. $C_9H_{16}O_3$. Calculated %: C 62.79; H 9.30.

SUMMARY

Well-crystallizing cyclohexlidene derivatives of l-arabinose, d-xylose, l-sorbose, mannite, dulcite and glycerine (liquid), not described in the literature, have been synthesized.

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CONVERSION AND SYNTHESIS OF CARBOHYDRATES

X. SYNTHESIS OF *d*- AND *l*-LYXOFLAVINS

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Of the many flavins which have been synthetically prepared, only some of the simple riboflavin analogs possessed an activity partially equivalent to that for Vitamin B_2, other flavins possessing no vitamin activity at all, or only to a negligible degree. Of the natural flavins, only *d*-riboflavin was known until very recently; a publication came out not long ago, however, [1], concerning the isolation of *l*-lyxoflavin from human heart muscle.

Of the stereoisomers of riboflavin, lyxoflavin was synthesized back in 1935 [2], and its optical antipode, *l*-lyxoflavin, was synthesized in 1949 by condensing *l*-lyxose with 2-amino-4,5-dimethyl-1-carboethoxyaminobenzene to give its N-glucoside, with subsequent reduction to the corresponding lyxamine, followed by hydrolysis of this compound and condensation with alloxane [1]. *d*-Lyxoflavin was obtained from *d*-lyxose through the same procedure.

It was determined in preliminary experiments that *l*-lyxoflavin in stimulating growth possesses a vitamin activity which differs from riboflavin activity [3]. It is possible that lyxoflavin is a special vitamin for heart muscle; it was, therefore, of interest to synthesize *d*- and *l*-lyxoflavin, and to study their biological activity.

Since the lyxoflavin molecule can be pictured as consisting of three bound parts – aromatic, aliphatic and pyrimidine – construction of the flavin molecule, therefore, can be carried out by combining the aromatic and aliphatic parts, and then with subsequent condensation of the aromatic polyhydroxyalkylamine with the pyrimidine part.

Upon condensing *l*-lyxose with 3,4-dimethylaminobenzene, according to the Sorokin reaction [4], by boiling in anhydrous alcohol, N-lyxofuranoside (I) was formed, which, in the presence of nickel catalyst, was converted into 3,4-xylyl-lyxamine (II), with m.p. 148-148.5°. Compared with other stereoisomeric glucamines, 3,4-xylyl-*l*-lyxamine possesses very low solubility in cold alcohol, and some solubility in hot alcohol. Its optical antipode resulted, with a m.p. of 150-151°, and the racemate with m.p. 131-132°.

Another nitrogen atom is introduced into the ortho-position to the existing one (which is necessary for the subsequent condensation with the pyrimidine part) of the 3,4-xylyl-lyxamine molecule (II). For this purpose, activity of the hydrogen atom in position 6 is used, which exceeds considerably the mobility of hydrogen in position 2; upon coupling of 3,4-xylyl-lyxamine with phenyldiazonium salts the azo group, therefore, enters principally at position 6, with formation of azolyxamine (III). As was demonstrated in the previous communication [5], optimal conditions for azo coupling of *d*-lyxamine lie in the range of pH 3-4; in this case, formation of diazoimino compound is excluded; azo coupling for the *l*-form was carried but by the authors.

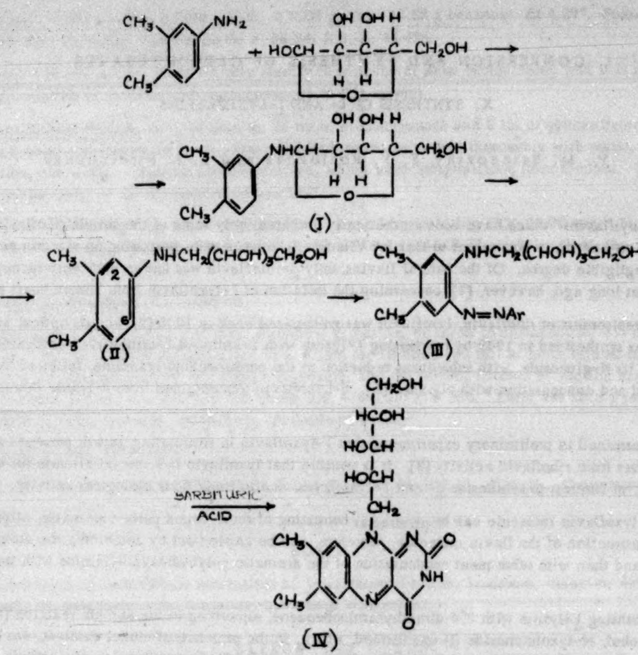
6-Phenylazo-3,4-xylyl-1-*l*-lyxamine (III) crystallized from 60% alcohol in the form of orange-red needles with m.p. 134-135°. Melting point of the *d*-form was 136.5-137.5°.

One of the proofs of structure for the azo dyes is the identity of their absorption spectra in the ultraviolet and visible ranges with the absorption spectrum for 6-phenylazo-3,4-xylyl-1-*d*-ribamine: I maximum 246 mμ, $\epsilon = 1.7 \cdot 10^4$; II maximum 325 mμ, $\epsilon = 1.99 \cdot 10^4$; III maximum 471 mμ, $\epsilon = 1.16 \cdot 10^4$. Additional proof that the azo group is in position 6 is the synthesis of corresponding lyxoflavins from azo dyes upon condensation with barbituric acid, as contrasted with the known fact that the stereoisomeric 2-phenylazo-3,4-xylyl-*d*-ribamine does not enter into condensation with barbituric acid [6].

For synthesis of *l*-lyxoflavin (IV) from the azo dye (III) and barbituric acid, as well as for synthesis of the optical antipode, N-butyl alcohol was used [7] as the medium. Purification of the flavins was carried out by reprecipitation from hydrochloric acid solutions, using hydrogen peroxide for oxidation of the reduced forms of the flavins [8].

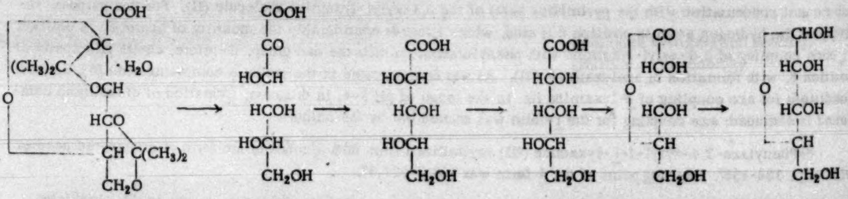
d-Lyxose, necessary for synthesis of *d*-lyxoflavin, was prepared by the authors according to the following scheme:

$$\textit{d}\text{-galactose} \xrightarrow{\text{oxidation } Br_2 + H_2O} \textit{d}\text{-galactonic acid} \xrightarrow{CaCO_3} \text{calcium } \textit{d}\text{-galactonate} \xrightarrow{H_2O_2\text{oxidation}} \textit{d}\text{-lyxose};$$



Upon oxidizing the calcium salt of galactonic acid with hydrogen peroxide in the presence of trivalent iron salts, using optimal conditions for the reaction [9], there resulted d-lyxose in 39% yield.

l-Lyxose was obtained according to the following scheme:



Diacetone-2-keto-l-gulonic acid (V)* was used as the starting product. Hydrolysis of (V) to the 2-keto-l-gulonic acid (VI), by heating its aqueous solution, took place in 76-82% yield [11]. 2-Keto-l-gulonic acid (VI), however, can be prepared directly from l-sorbose in about 50% yield by oxidation of the latter with air in sodium bicarbonate solution in the presence of platinum or palladium catalyst [12]. The oxidative rupture of 2-keto-l-gulonic acid with hydrogen peroxide into l-xylonic acid (VII) proceeds with rupture of the l-carbon, in 24% yield [13].

The authors obtained l-xylonic acid (VII) in 75% yield by direct hydrolysis of diacetone-2-keto-l-gulonic acid (V), and by oxidation with hydrogen peroxide (with 2 atoms of active oxygen). l-Xylonic acid was epimerized in the presence of organic bases to l-lyxonic acid (VIII), but not with free acid [13], although indirectly with its complex cadmium salt with cadmium bromide, an extension in this case of the procedure of epimerization of aldonic acids in the form of their salts [14]. Transition to epimeric l-lyxonic acid was 40-50%.

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* Prepared from l-sorbose via diacetone-l-sorbose in 60-65% yield [10].

The l-lyxono-γ-lactone (IX) was obtained from l-lyxonic acid (VIII) by heating in vacuo the syrupy acid left after evaporation and removal of the cadmium ions from the cadmium salt solution. Complete elimination of bromide salts was not carried out, since their presence did not interfere with electrolytic reduction at the mercury cathode, which the authors used for conversion of l-lyxono-γ-lactone (IX) into l-lyxose (X).

Since the resulting l-lyxose could have contained impurities of the stereoisomeric l-xylose, formed because of the xylonic acid impurity present, it was, therefore, important to study the properties of the product formed from xylose, namely, 3,4-xylylxylamine, and to clarify the possibility of its purification from 3,4-xylyllyxamine. A study of the properties of 3,4-xylylxylamine was carried out with its d-optical antipode. The crystalline compound failed to separate from the condensation product of d-xylose with 3,4-dimethylaminobenzene after its reduction to 3,4-xylyl-d-xylamine; after evaporation of the solutions, a non-crystallizing gelatinous residue remained. Upon azo coupling of this product with the phenyldiazonium salts, there was obtained 6-phenylazo-3,4-xylyl-1-d-xylamine with m.p. 139.5-140° [5] (found %: N 11.81; calculated %: N 11.69) and with an absorption spectrum of: I maximum 246 mμ, II maximum 325 mμ, III maximum 471 mμ, which was identical with the absorption maxima for the stereoisomeric azoribamine. Subsequently, the authors succeeded in crystallizing 3,4-xylyl-d-xylamine (upon prolonged standing) and in purifying it partially.

It was thus established that lyxamine can be readily purified from its impurity of stereoisomeric xylamine on the basis of their widely varying solubilities in water and alcohol.

While completing the present investigation, synthesis of the l-form of lyxoflavin was published [15], but without isolation of the dye in the pure state; the authors started with galacturonic acid in order to obtain l-lyxose.

EXPERIMENTAL

Synthesis of 3,4-Xylyl-d-xylamine

4 g of recrystallized d-xylose with m.p. 149-150°, 3.2 g of 3,4-dimethylaminobenzene and 40 ml of anhydrous alcohol were heated on a water bath for 40 minutes, under reflux, to complete dissolution. The resulting N-glucoside solution was hydrogenated in a rotating autoclave over nickel catalyst at 40 atms, and a temperature of 65-70° for 2 hours. After filtration, the solvent was distilled off from solution. Syrup resulted in the residue, which, upon prolonged standing, crystallized. After washing with hot acetone, and crystallizing from a small amount of N-butyl alcohol-acetone mixture (2:3), there resulted 3,4-xylyl-d-xylamine in the form of colorless clusters of thin needles with m.p. 129-130°. The product was very soluble in ethyl alcohol and water.

6.100 mg sub.: 0.270 ml N_2 (19°, 548 mm). Found %: N 5.08. $C_{13}H_{21}O_4N$. Calculated %: N 5.48.

Synthesis of d-Lyxoflavin

Calcium d-galactonate. 120 g of d-galactose was dissolved in 500 ml of water, 45 ml of bromine added, and after complete dissolution of bromine, it was left to stand for 48 hours in darkness. Bromine excess was then removed from the warm solution by air-blowing, 90 ml of 40% sodium hydroxide added, and then 40 g of chalk; after heating on a boiling water bath for 1.5 hours, the mixture was filtered. After cooling, crystallization began; the precipitate was filtered and washed with 30% alcohol. 117 g of calcium galactonate resulted, and then after evaporation of the solution twice, another 18 g resulted; yield was 77.7%.

d-Lyxose. 80 g of calcium d-galactonate was dissolved in 1,000 ml of hot distilled water, and it was then mixed with a solution of 1.4 g of ferric sulfate [$Fe_2(SO_4)_3 \cdot 9H_2O$] in 12 ml of water, and 2 g of barium acetate in 12 ml of water. 80 ml of 30% hydrogen peroxide diluted with 200 ml of water was added uniformly to the mixture at 60° over a period of 1.5 hours. Several minutes following start of addition of hydrogen peroxide, evolution of carbon dioxide. After a half-hour addition of the total quantity of hydrogen peroxide, and cessation of the gas evolution, the mixture was filtered, and the solution evaporated in vacuo to a volume of 80 ml at a bath temperature of not over 60°. 480 ml of methyl alcohol was added to the residue with stirring, and then 320 ml of acetone at room temperature. After 5 minutes, the resulting precipitate was filtered off, washed with methyl alcohol, and the filtrate evaporated in vacuo to the consistency of syrup. 26.6 g of syrup resulted, with a content of 62.8% lyxose; yield was 39%.

3,4-Xylidine-N-d-lyxofuranoside. A mixture of 4 g of d-lyxose, 3.2 g of 3,4-dimethylaminobenzene and 60 ml of anhydrous alcohol was heated with reflux condenser on a water bath for 15-20 minutes to complete dissolution. A crystalline precipitate separated, which was filtered off and washed with alcohol. 5.75 g (85%) of 3,4-xylidine-N-d-lyxofuranoside in the form of colorless platelets resulted, with m.p. 146-147°.

3.040 mg sub.: 6.840 mg CO_2; 1.935 mg H_2O. 3.915 mg sub.: 0.147 ml N_2 (24°, 746 mm). Found %: C 61.35; H 7.10; N 5.02. $C_{13}H_{19}O_4N$. Calculated %: C 61.64 H 7.56; N 5.53.

3,4-Xylyl-d-lyxamine. 3.3 g of the prepared N-glucoside and 70 ml of anhydrous alcohol were hydrogenated in a rotating autoclave in the presence of nickel catalyst under a pressure of 40 atms and 65-70° for 2 hours. After decanting off the hot alcoholic solution from the catalyst, and cooling, a compound separated which was recrystallized from water. 2.5 g (74%) of 3,4-xylyl-d-lyxamine resulted in the form of lustrous needles.

M.p. 150-151°, $[\alpha]_D^{20}$ + 31.5° (concentration of 5% in 2 N HCl).

5.411 mg sub.: 0.263 ml N_2 (22°, 745 mm). Found %: N 5.51. $C_{13}H_{21}O_4N$. Calculated %: N 5.48.

6-Phenylazo-3,4-xylyl-1-d-lyxamine. 1 g of lyxamine was dissolved in 100 ml of hot water, 0.5 ml of pure hydrochloric acid added, and carefully, to avoid crystallizing, cooled to 20-25°. The lyxamine solution was added with stirring to a diazonium salt solution prepared from 0.46 g of aniline, 0.66 g of sulfuric acid and 0.34 g of sodium nitrite. The azo coupling was carried out at 18-20° and at a pH of 3.8-4.0, attained by addition of 15% sodium acetate solution, and then maintained so for the 3-hour period. The resulting precipitate was filtered off, washed with water, and dried in air. 1.14 g (80.8%) of the azo dye was obtained, with a m.p. of 105-110°. The crude compound dissolved very readily in organic solvents — alcohols, benzene, chloroform, acetone and others. To purify it, the substance was dissolved in alcohol, filtered from impurities, and left for slow crystallization with the solvent evaporated almost to dryness. The residue was washed on a filter with 50% alcohol, and recrystallized several times from a small amount of 50-60% alcohol. 6-Phenylazo-3,4-xylyl-1-d-lyxamine resulted in the form of long needle clusters, red in color, with m.p. 136-136.5°, or with rapid crystallization, in the form of separate, thin needles, orange-red in color, with m.p. 136.5-137.5°.

4.593 mg sub.: 0.462 ml N_2 (22°, 746 mm). Found %: N 11.43. $C_{19}H_{25}O_4N_3$. Calculated %: N 11.69.

d(+)-Lyxoflavin. A mixture of 0.5 g of azolyxamine, 0.3 g of barbituric acid, 6 ml of n-butyl alcohol and 1 ml of glacial acetic acid was heated with reflux condenser on a boiling water bath for 5 hours with stirring. There gradually accumulated on the wall of the flask a dark-yellow precipitate, which, after termination of reaction, was filtered off, washed with butyl alcohol, and then with boiling water. 0.25 g of crude d-lyxoflavin resulted. It was dissolved in 1 ml of pure hydrochloric acid, and after complete dissolution 1 ml of water and 2 drops of hydrogen peroxide were added. The solution was filtered and poured into 6 ml of hot water. The resulting precipitate was stirred in the hot state for several hours, d-Lyxoflavin was obtained in the form of yellow needles with m.p. 276-278° (with decomposition).

$[\alpha]_D^{20}$ + 46° ± 5° (concentration 0.25% in 0.05 N NaOH). The absorption spectrum possessed maxima at 445, 370, 265 and 222 mμ. Found %: N 14.43, 14.44. $C_{17}H_{20}O_6N_4$. Calculated %: N 14.90.

Synthesis of 1-Lyxoflavin

1-Xylonate cadmium-cadmium bromide $[C_5H_9O_6)_2Cd \cdot CdBr_2 \cdot 2H_2O]$. 200 g of diacetone-2-keto-1-gulonic acid (hydrated) (V) was dissolved in 600 ml of distilled, boiling water and for the hydrolysis, was boiled for 40 minutes. The solution was then neutralized with 40 g of sodium carbonate and oxidized at 0° by adding 160 ml of 30% perhydrol for 1 hour. After completion of the oxidation, the solution was acidified with hydrochloric acid (d 1.19) and evaporated to a syrup in vacuo. The residue was diluted with 300 ml of water and treated with 65 g of cadmium carbonate, heating to boiling. After cessation of the foaming, the excess cadmium carbonate was filtered off and the filtrate poured into a solution of aqueous cadmium bromide. After cooling, crystallization started. The precipitate was filtered off on the following day and washed with ice water. 192 g (75%) of the double cadmium salt of 1-xylonate resulted.

Found %: Cd 29.73. $C_{10}H_{18}O_{12}Br_2Cd_2 \cdot 2H_2O$. Calculated %: Cd 29.95.

1-Lyxono-γ-lactone (IX). 1-Xylonic acid (VII) was epimerized directly into 1-lyxonic acid (VIII), the former being in the form of the double salt, 1-xylonate cadmium-cadmium bromide, from which resulted 1-lyxono-γ-lactone upon treating the cadmium salt with hydrogen sulfide, following by heating of the evaporated residue in vacuo.

40 g of the double salt, 500 ml of water and 50 ml of pyridine were placed in a rotating autoclave; epimerization was carried out for 5 hours at a temperature of 144-146°, air being displaced by nitrogen. A mixture consisting of the solution and the complex compound of cadmium bromide with pyridine ($CdBr_2 \cdot C_5H_5N$), was removed, and the pyridine distilled out with steam; thereupon, the precipitate gradually went into solution. The solution was filtered while hot and the filtrate evaporated in vacuo to 50 ml, whereupon a crystalline precipitate of the double salt separated; it was filtered off after cooling. The xylonate cadmium-cadmium bromide recovered from the reaction was about 15-20 g. After dilution of the filtrate with 100 ml of water, the cadmium was precipitated with hydrogen sulfide. The cadmium sulfide precipitate was filtered off, the solution of 1-lyxonic acid clarified with

activated charcoal and heat, and after filtration, it was evaporated in vacuo to 50 ml. The residue was neutralized with sodium hydroxide to a pH of 2.5, and after filtration, and second clarification, using activated charcoal, it was evaporated to a syrup in vacuo, which was kept on a boiling water bath in vacuo for 2 hours. 36 g (65%) of crude l-lyxono-γ-lactone was obtained from 140 g of xylonate which entered into reaction (from several experiments).

l-Lyxose (X). l-Lyxono-γ-lactone was converted into l-lyxose by electrical reduction on a mercury cathode. An electrolyzer with membrane was used. 10% sulfuric acid served as anolyte, lead being used for the anode. The catholyte contained 10% lactone and 10% sodium sulfate. Electrolysis was carried out at 13-15°, and 5-6 V. Stirring was continued for the duration of electrolysis, and the pH kept at a level of 3.5-4.5. After termination of reduction, l-lyxose solution containing sodium sulfate and aldonic acid salts was evaporated in vacuo (bath temperature 50°) to 70 ml volume.

350 ml of methyl alcohol was added to the residue, and the sodium sulfate which separated was filtered off and washed with methyl alcohol. The filtrate was evaporated in vacuo to 60 ml, diluted with water to 180 ml, and treated with excess barium carbonate, and stirring, on a boiling water bath for 30 minutes. After filtration, the solution was evaporated in vacuo to a thin syrup, which was again treated with methyl alcohol, with stirring. The precipitate which separated was filtered off and the solution again evaporated to a syrup. 15 g of syrup, with 6 g of l-lyxose content, resulted.

3,4-Xylyl-l-lyxamine (II). 5 g of l-lyxose and 4 g of 3,4-dimethylaminobenzene in 60 ml of anhydrous alcohol was condensed to 3,4-xylidine-N-l-lyxofuranoside (I), by heating on reflux and a water bath for 30 minutes. The N-glucoside solution which resulted was hydrogenated in a rotating autoclave with nickel catalyst at 70° and 40 atms for 2 hours. The hot solution was decanted from the catalyst and then filtered. The resulting precipitate was recrystallized from water. 3.6 g (42%) of 3,4-xylyl-l-lyxamine in the form of colorless needles with m.p. 148-148.5° resulted (m.p. 147-148° according to the literature data [15]).

$[\alpha]_D^{20}$ −32.5° (concentration 2% in 2 N HCl). Found %: N 5.55. $C_{13}H_{21}O_4N$. Calculated %: N 5.48.

3,4-Xylyl-dl-lyxamine. Obtained by mixing solutions of optical antipodes in the form of needles with m.p. 131-132° (from alcohol). Recrystallization did not increase the melting point.

6-Phenylazo-3,4-xylyl-1-l-lyxamine (III). Prepared from lyxamine (II) by the same procedure as for its optical antipode. The azo dye crystallized from aqueous alcohol in the form of red needles with m.p. 134-135°.

3.686 mg sub.: 0.382 ml N_2 (19°, 741 mm). Found %: N 11.79. $C_{19}H_{25}O_4N_3$. Calculated %: N 11.69.

l-Lyxoflavin (IV). Prepared from azolyxamine (III) and barbituric acid in the presence of acetic acid in n-butyl alcohol medium by the same procedure as was described for its optical antipode. l-Lyxoflavin was in the form of yellow needles with m.p. 277-279°.

$[\alpha]_D^{20}$ −45° ± 5° (concentration 0.4% in 0.05 N NaOH).

Its absorption spectrum, from the extinction values and from the maxima (λ = 445, 370, 265 and 222 mμ) was identical to the absorption spectra for d-lyxoflavin and d-riboflavin.

Found %: N 14.32. $C_{17}H_{20}O_6N_4$. Calculated %: N 14.90.

SUMMARY

1. Synthesis of l-lyxose from diacetone-2-keto-l-gulonic acid by a series of conversions has been attained. Epimerization of l-xylonic acid has been carried out in the form of its double cadmium salt. l-Lyxonic acid has been converted into l-lyxose by lactonization and electrolytical reduction on a mercury cathode.

2. d- and l-lyxoflavins have been synthesized by condensing lyxose with 3,4-dimethylaminobenzene, reduction of the resulting N-glucoside to lyxamine, its azo coupling, and condensation of the azo dye with barbituric acid.

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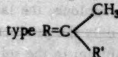
INVESTIGATIONS IN THE FIELD OF TAUTOMERIC COMPOUNDS

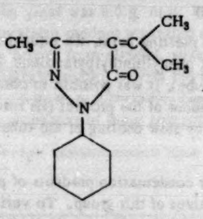
XV. INTERACTION OF PHENYLMETHYLPYRAZOLONE WITH KETONES

A. E. Porai-Koshits* and M. S. Dinaburg

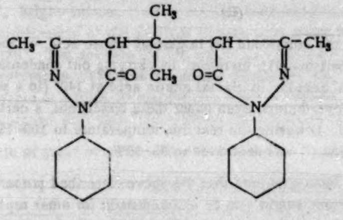
As one of the authors has demonstrated with N. V. Khromov [1], the condensation products for a number of iso-oxazolone derivatives with ketones, of the type  $R{=}C\langle^{CH_3}_{R'}$, where R is the isooxazolone radical, and R' equals CH_3, or aryl, possess high mobility of the hydrogen atoms in the methyl groups. This mobility is evidenced in their ability to enter into reaction with aldehydes and diazo- and nitro- compounds, which lead to new compounds of interest from both a theoretical and a practical viewpoint. Condensation products of phenylmethylpyrazolone with ketones, constructed according to the type indicated (where R = the phenylmethylpyrazolone radical, and R' is CH_3 or aryl) should also possess analogous properties.

Because of the fact that literature data on synthesis of similar-type compounds are very meager, and are for the most part limited to an early work by Knorr [2], the authors considered it necessary to carry out a thorough research on their properties and methods of synthesis.

As is known, Knorr obtained condensation products of phenylmethylpyrazolone with acetone (I) and (II):



(I)



(II)

The structures of these compounds have subsequently been quite convincingly proved [3, 4]; a thorough study of their chemical properties and conversions, however, was not carried out.

Early investigation of the synthesis of substance (I) brought to light the fact that it always resulted in a mixture with (II), the amount of latter depended upon the excess of acetone taken, and rapidly increased (compound II) when acetone was in slight excess. At the same time, large acetone excess had very little effect upon increasing the yield of (I). Isopropylidenephenylmethylpyrazolone (I) converted with great ease into the compound (II) when reacted with phenylmethylpyrazolone in alcoholic solution, or by direct melting of the initial compounds.

Conversion of compound (II) into (I), when reacted with acetone, did not occur, as might be expected according to the scheme

$$(II) + CH_3{-}CO{-}CH_3 \rightarrow 2\,(I),$$

because of which fact accumulation of compound (II) occurred in the reaction mass.

Isopropylidenephenylmethylpyrazolone (I) is noted by its instability, especially when reacted with compounds of basic nature. Even upon short heating in alcohol, containing traces of alkali hydroxide, sodium carbonate or sodium acetate, it converted almost completely into (II), apparently as a result of reaction

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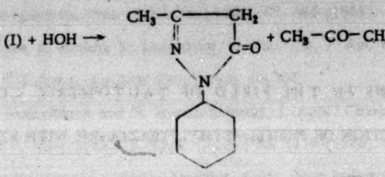
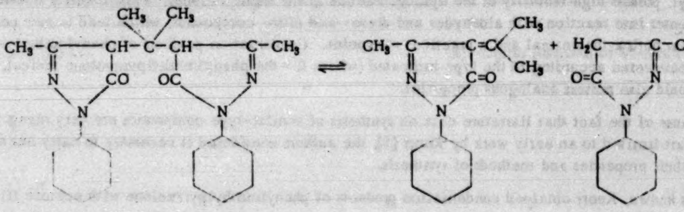
* Deceased.



with subsequent interaction of the initial product with the phenylmethylpyrazolone formed. On the other hand, compound (II) is stable to the action of bases and caustic alkali. Its solutions in alkalies can be stored for a long time without noticeable decomposition. When boiled in alcohol, however, it decomposed partially into phenylmethylpyrazolone and isopropylidenephenylmethylpyrazolone; the latter could be isolated by rapid cooling of the solution. They both interacted with each other, and only the product (II) separated on gradual cooling of the alcoholic solution. Consequently, there existed an equilibrium in the solution:

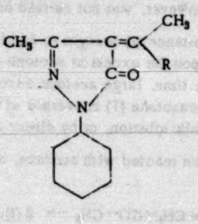


(II) (I)

Upon heating the compound (II) in glacial acetic acid, or above its melting point, the equilibrium was shifted to the right (see experimental); therefore, by carrying out condensation of phenylmethylpyrazolone with an equimolecular amount of acetone in glacial acetic acid at 140° (in a sealed tube), it was possible to obtain up to 70-75% of compound (I). Nevertheless, even under these conditions, a certain amount of the product (II) resulted, chiefly by cooling the tubes. Lowering the reaction temperature to 100-110°, or by slow cooling of the tubes in an oven, the yield of compound (I) was decreased to 35-40%.

It could have been expected that the above-described properties for condensation products of phenylmethylpyrazolone with acetone would also be characteristic for other representatives of this group. To verify this assumption, the reactions of phenylmethylpyrazolone with acetophenone and m-nitroacetophenone were studied.

Acetophenone and m-nitroacetophenone entered into reaction with phenylmethylpyrazolone, forming derivatives not described in the literature, whose structure and properties correspond to the formula (III):



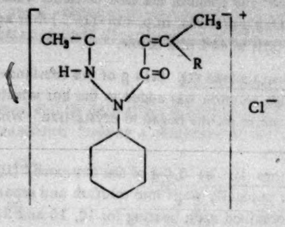
(III)

where R = C_6H_5 or m-$C_6H_4NO_2$.

It is characteristic that in this case no products similar to compound (II) were formed according to our observations. In contrast to the acetone analog these compounds did not enter into reaction with phenylmethylpyrazolone, and a product similar to compound (II) failed to form, even when using a very large excess of phenylmethylpyrazolone, and under a large variety of conditions for the reaction course.

Acetone, acetophenone and m-nitroacetophenone derivatives constructed according to type (I), displayed clearly amphoteric properties.

Thus, on the one hand, they are all capable of adding hydrogen chloride, apparently thanks to the imino nitrogen of the pyrazolone ring, forming salts, the structure of which can be represented by the formula:



These salts are very unstable and in the air lose hydrogen chloride immediately, converting into the initial bases. They can be kept for a long time in crystalline form in anhydrous ether with hydrogen chloride. On the other hand, they are soluble in alkali. While isopropylidenephenylmethylpyrazolone dissolves in alcoholic alkali and disintegrates rapidly, acetophenone and m-nitroacetophenone derivatives form stable alkaline solutions, from which they can be isolated by acidification. The latter of these products possess such a well-defined acid character, that it dissolved even in dilute aqueous alkali.

EXPERIMENTAL

Condensation of phenylmethylpyrazolone with acetone, according to Knorr. 17.4 g (0.1 mole) of phenylmethylpyrazolone and 57 g (1.0 mole) of acetone were heated under reflux on a water bath for 6 hours. After 12 hours, the resulting precipitate was filtered off and washed with acetone, dilute alkali, water, and dried in a desiccator. The yield was 9.5 g, m.p. 114-115°, Bright-yellow, lustrous crystals from alcohol, m.p. 116-117°. The white crystalline product separated upon acidification of the alkaline filtrate with dilute HCl. Yield was 1.35 g. White prisms from alcohol, with m.p. 138°. The acetone mother liquor was diluted with water, the resulting precipitate treated as with the basic precipitate. Yield of the yellow compound was 0.87 g, m.p. 104-109°; white, 8.10 g, m.p. 129-130°. The total yield of yellow compound was 10.37 g (46.8%), and of white, 9.45 g (48.7%). The properties of these compounds coincided with those indicated in the literature [2, 3, 4].

The effect of acetone excess upon the ratio of yield of white and yellow products is given in the table.

TABLE

Moles taken for reaction		Mole ratio	Yield (%)	
phenylmethyl-pyrazolone	acetone		compound (I)	compound (II)
0.02	0.01	0.5	–	96.0
0.02	0.05	2.5	5.6	87.8
0.02	0.1	5	29.5	68.5
0.02	0.2	10	47.0	48.7
0.02	0.4	20	51.0	46.4
0.02	1.0	50	46.9	46.6

Condensation of isopropylidenephenylmethylpyrazolone with phenylmethylpyrazolone. a) 2.14 g (0.01 mole) of compound (I), 1.75 g of phenylmethylpyrazolone, and 10 ml of methyl alcohol were heated under reflux. After 30 minutes, white crystals began to separate. After 12 hours, the precipitate was filtered and washed with ether. White lustrous prisms (from alcohol), m.p. 138°. Yield was 3.8 g (96%). There was no depression in melting point of the mixture when mixed with the white compound prepared according to the method of Knorr.

b) 2.14 g of the substance (I) and 1.75 g of phenylmethylpyrazolone were mixed thoroughly in a reaction flask at 100°. The yellow melt which formed at the beginning soon solidified to a solid white mass. Heating was continued for 3 hours, and then the melt was powdered in a mortar, and washed with ether. The yield of white product was 3.07 g (77.5%). From alcohol – white crystals with m.p. 138°.

Rupture of the white compound. 1.94 g of the white compound (m.p. 138°) was heated with 10 ml of ethyl alcohol for 30 minutes. The solution was cooled rapidly with salt-ice mixture. A bright-yellow crystalline precipitate separated immediately. The yield was 0.4 g. Bright-yellow needles with m.p. 117° from glacial acetic acid. A small amount of white crystals with m.p. 136-137° precipitated from the alcoholic mother liquor upon standing, after separation of the yellow crystals. After their separation, the filtrate was heated to boiling and diluted with 15 ml of water. The remaining white compound separated in the form of an oil. Phenylmethylpyrazolone (m.p. 122-124°) precipitated in the form of long, white needles from the water-alcoholic solution upon cooling. Only the white compound precipitated upon slow cooling of the alcoholic solution.

Synthesis of isopropylidenephenylmethylpyrazolone in glacial acetic acid. 17.4 g of phenylmethylpyrazolone, 15 ml of acetone (13.0 g) and 15 ml of glacial acetic acid were heated in a sealed tube at 140° for 6 hours. The tube was cooled as rapidly as possible to 40-50° and opened; the tube contents were transferred to a beaker, where it crystallized immediately. The yield was 15.2 g (71.0%), m.p. 115-116°. From acetic acid – needles with m.p. 117°. If the tube is cooled slowly, the yield falls to 44% and below.

Rupture of isopropylidenephenylmethylpyrazolone (I). 2.14 g of the substance (I) was heated with 10 ml of 95% alcohol. 2 drops of 0.5% sodium hydroxide solution was added to the hot solution. The solution turned to a red-brown color and after 2-3 minutes, fine, white prisms began to crystallize. White prisms with m.p. 138° from alcohol.

Attempt to convert the compound (II) into (I). a) 3.0 g of the compound (II) was boiled with 15 ml of acetone under reflux for 2 hours. The precipitate gradually went into solution and separated upon cooling. White prisms with m.p. 136°. A similar result was obtained upon heating for 10, 15 and 30 hours.

b) 3.0 g of compound (II) and 30 ml of acetone were heated in a sealed tube at 120° for 2 hours. The initial compound reprecipitated.

Condensation of phenylmethylpyrazolone with acetophenone (4-α-phenylethylidenephenylmethylpyrazolone). 17.4 g (0.1 mole) of phenylmethylpyrazolone and 12.0 g (0.1 mole) of acetophenone in a flask equipped with air condenser were heated in an oil bath at 100°, everything passing into solution, and at 145° an intense evolution of water beginning. After 3 hours, the mass was transferred to a beaker and stirred vigorously with a rod to the start of crystallization; after 1.5-2.5 hours, the mass solidified. After 12 hours, it was ground in a mortar with 100 ml of gasoline (b.p. 70-90°), separated, washed on a filter with 100-150 ml of gasoline and 25-30 ml of methyl alcohol; afterwards, it was washed in a beaker with dilute alkali solution (~ 5-10 %), water and dilute acetic acid. Yellow prisms with m.p. 88-89° from ethyl alcohol. Yield of pure product 17.9 g (65%). Soluble in alcohol, acetone, ether, glacial acetic acid. Insoluble in ligroin and petroleum ether.

0.1506 g sub.: 13.2 ml N_2 (21°, 776 mm). 0.0840 g sub.: 7.3 ml N_2 (21°, 780 mm). 0.1740 g sub.: 0.4985 g CO_2; 0.0985 g H_2O. 0.1518 g sub.: 0.4361 g CO_2; 0.0820 g H_2O. Found %: C 78.27, 78.32; H 6.20, 6.01; N 10.34, 10.30. $C_{18}H_{16}ON_2$. Calculated %: C 78.26; H 5.79; N 10.14.

Condensation of phenylmethylpyrazolone with m-nitroacetophenone (3-nitrophenyl-4-α-ethylidenephenylmethylpyrazolone). 7.0 g of phenylmethylpyrazolone and 6.6 g of m-nitroacetophenone were placed in a flask equipped with reflux condenser in an oil bath heated at 150°. Reaction began immediately, as noted by the evolution of water. The melt was cooled and ground thoroughly with 10 ml of glacial acetic acid. After a given time, all the mass had crystallized. The precipitate was filtered off, washed with a small amount of acetic acid, and then with ether. Yield was 4.5-5.0 g (35-40%). The compound was soluble in toluene, xylene, glacial acetic acid, poorly so in benzene, very poorly so in ethyl and methyl alcohols and acetone, and insoluble in ether. Yellow prisms from 85% acetic acid, with m.p. 150-151°.

0.1004 g sub.: 11.4 ml N_2 (22°, 762 mm). 0.1029 g sub.: 0.2541 g CO_2; 0.0456 g H_2O. Found %: C 67.39; H 4.96; N 13.17. $C_{18}H_{15}O_3N_3$. Calculated %: C 67.29; H 4.98; N 13.08.

Attempt at condensation of 4-α-phenylethylidene- and 3'-nitrophenyl-4-α-ethylidenephenylmethylpyrazolones with phenylmethylpyrazolone. Attempts to effect this reaction, carrying out at various temperatures and duration times for the experiments, heating in solvents, or melting, with various amounts of initial compounds and various temperatures, were of no avail. In all cases, the reaction mass converted into the original compounds.

Reaction of alkali with 4-α-phenylethylidenephenylmethylpyrazolone. 2.76 g of the compound was dissolved in 15 ml of ethyl alcohol and 5 ml of 20% sodium hydroxide added to the solution. The orange-red solution did not change color on boiling. The solution was diluted with water to 250 ml and acidified with dilute hydrochloric acid. The resulting precipitate was filtered off, washed with water, and recrystallized from ethyl alcohol. Yellow crystals with m.p. 87-88°. Boiling the alkaline solution for 5 hours produced decomposition of the compound and a pronounced odor of acetophenone was apparent.

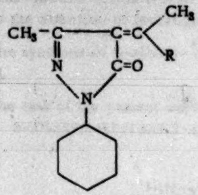
Alkaline reaction with 3'-nitrophenyl-4-α-ethylidenephenylmethylpyrazolone. 0.3 g of the compound was dissolved, in the cold, in 50 ml of 0.1 N sodium hydroxide solution. From the yellowish solution, the initial product was isolated in the form of a yellowish, flaky precipitate by means of carbon dioxide.

Reaction of dry hydrogen chloride with 4-isopropylidene-4-α-phenylethylidene- and 3'-nitrophenyl-4-α-ethylidenephenylmethylpyrazolone. 2.14 g of 4-isopropylidenephenylmethylpyrazolone was dissolved in 25 ml of anhydrous ether and dry hydrogen chloride passed into the solution. Separation of a colorless oil began immediately, which, when rubbed with a rod, solidified to a colorless, crystalline mass. The crystals were stable in saturated hydrogen chloride, and when separated from the liquid, they immediately melted to a brown resinous mass, which crystallized with difficulty.

4-α-Phenylethylidene- and 3'-nitrophenyl-4-α-ethylidenephenylmethylpyrazolone behave similarly, with the difference that the oil separating upon decomposition of the hydrochloride crystallizes more readily.

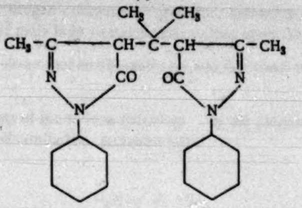
SUMMARY

1. Acetone, acetophenone and its derivatives substituted in the ring, enter into reaction with one or two molecules of phenylmethylpyrazolone, forming a compound of the type:



(I)

or



(II)

where R equals aromatic or aliphatic radical.

2. The dominant direction of the reaction depends upon the nature of reacting ketone. Thus, with acetone, approximately equal amounts of compounds (I) and (II) are formed, while acetophenone and m-nitroacetophenone produce only interaction products with one molecule of phenylmethylpyrazolone.

3. The formation of a mixture of compounds in the case of phenylmethylpyrazolone interaction with acetone is explainable by the ability of a compound of type (I) formed, to react in turn with phenylmethylpyrazolone, forming compound (II).

4. Compounds of type (I) possess definite amphoteric properties.

LITERATURE CITED

[1] A. E. Porai-Koshits and N. V. Khromov, J. Gen. Chem., 10, 1829 (1947).

[2] Knorr, Ann., 238, 179 (1887).

[3] Pauly, Ber., 30, 484 (1897).

[4] Stolle, Ber., 38, 3028 (1905).

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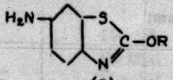
2-ALKOXYMETHYL- AND 2-ARYLOXYMETHYL-6-AMINOBENZTHIAZOLES

S. G. Fridman

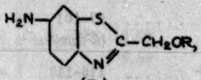
Alkoxyamino derivatives of heterocyclic nitrogen compounds – pyridine, quinoline, benzthiazole – attracted long ago the attention of investigators because of their high bacteriostatic action upon the tuberculosis bacillus [1].

The synthesis of 2-alkoxy- and 2-aryloxy-6-aminobenzthiazoles (I) was described in the author's preceding work [2].

The task of the present work was a synthesis of methylene homologs of the preparations obtained earlier, namely: 2-alkoxymethyl and 2-aryloxymethyl-6-aminobenzthiazoles (II):



(I)

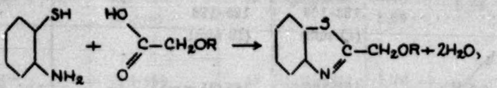


(II)

where R = alkyl, aryl or aralkyl.

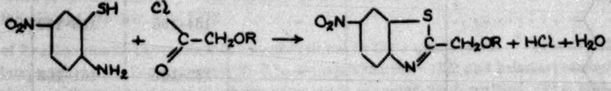
Synthesis of this type of compound can be attained in two ways.

I. Obtaining 2-alkoxymethylbenzthiazoles by condensation of o-aminophenylmercaptan with alkoxyacetic acids



and then nitrating the resulting bases.

II. Obtaining 2-alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles by condensation of 5-nitro-2-aminophenylmercaptan with the chloroanhydrides of alkoxy and aryloxyacetic acids according to the equation



The reduction of 6-nitro derivatives obtained by either method was expected to produce amines of interest to the author.

The initial materials required, namely aryloxyacetic acids, are described in the literature.

Constants, found by the author and found in the literature for alkoxy- and aryloxyacetic acids, which were used in the present work, are given in Table 1.

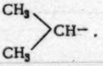
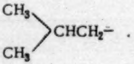
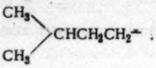
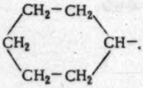
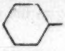
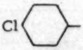
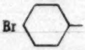
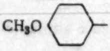
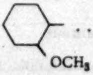
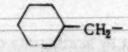
Condensation of o-aminophenylmercaptan with alkoxyacetic acid was carried out by heating the components at 135-140° for 3-4 hours. The 2-alkoxymethylbenzthiazoles synthesized by the author, are given in Table 2.

Preparations I and II given in Table 2 were synthesized by the same procedure as by other authors [14, 15]. V. M. Zubarovsky synthesized preparations III, V and IX by interacting 2-bromomethylbenzthiazole with the corresponding alcoholates [16].

2-Alkoxymethylbenzthiazoles are colorless liquids, with the exception of 2-isopropoxymethylbenzthiazole (IV), which had a m.p. of 39°, and 2-cyclohexyloxymethylbenzthiazole (VIII) with a m.p. of 59°.

TABLE 1

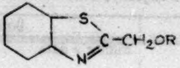
Alkoxy- and Aryloxyacetic Acids of the General Formula $ROCH_2COOH$

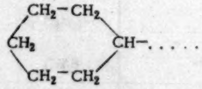
Preparation Number	R	Boiling point		Melting point		Yield (%)	Literature
		author's data	literature data	author's data	literature data		
I	CH_3-	197-198°	99-100° (25 mm)	–	–	53	[3]
II	CH_3CH_2-	97 (7 mm)	109-111 (17-18 mm)	–	–	70	[4]
III	$CH_3CH_2CH_2-$	110-112 (12 mm)	108 (10 mm)	–	–	61	[5]
IV	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>CH-$	97-101 (5 mm)	113 (21 mm)	–	–	49	[3]
V	$CH_3CH_2CH_2CH_2-$	115-117 (11 mm)	115-116 (10 mm)	–	–	72	[5]
VI	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>CHCH_2-$	107-108 (11 mm)	118 (18 mm)	–	–	87	[3]
VII	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>CHCH_2CH_2-$	235; 117-119 (5 mm)	235	–	–	83	[6]
VIII	$n-C_8H_{17}-$	163-166 (11 mm)	125-126 (12 mm)	–	–	63	[5]
IX		155-159 (20 mm)	165 (25 mm)	–	–	61	[7]
X	$CH_2=CH-CH_2-$	118-120 (10 mm)	120 (13 mm)	–	–	59	[8]
XI		–	–	99	99°	54	[9]
XII		–	–	154-155	155-156	78	[10]
XIII		–	–	160-161	161-162	51	[11]
XIV		–	–	111-112	110-112	49	[11]
XV		–	–	122-123	121	65	[12]
XVI		165 (5 mm)	136 (0.2 mm)	–	–	68	[13]

The reaction of nitric acid with alkoxyderivatives of heterocyclic nitrogen compounds has received but little study. It is known that upon nitrating benzyl alcohol esters, the nitro group moves chiefly to the p-position [17]. Isobutyl- and isoamyl-benzyl esters react with nitric acid (d 1.5) to form benzaldehyde and the corresponding alkyl nitrates [18].

TABLE 2

2-Alkoxymethylbenzthiazoles of the General Formula



Preparation Number	R	Boiling point	Yield (%)	Empirical formula	Analytical results			
					nitrogen (%)		sulfur (%)	
					found	calc'd	found	calc'd
I	CH_3-	135-138° (5 mm)	68	–	–	–	–	–
II	CH_3CH_2-...........	141-142 (7 mm)	58	–	–	–	–	–
III	$CH_3CH_2CH_2-$	151-152 (7 mm)	49	$C_{11}H_{13}ONS$	6.79 6.84	6.76	15.45 15.30	15.46
IV	$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>CH-$.........	150-152 (10 mm) M.p. 39°	60	$C_{11}H_{13}ONS$	6.69 6.52	6.76	15.30 15.40	15.46
V	$CH_3CH_2CH_2CH_2-$	163-164 (6 mm)	67	$C_{12}H_{15}ONS$	6.06 6.11	6.33	13.97 14.28	14.48
VI	$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>CHCH_2-$	133-134 (3 mm)	72	$C_{12}H_{15}ONS$	6.18 6.28	6.33	14.25 14.15	14.48
VII	$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>CHCH_2CH_2-$	151-152 (3 mm)	69	$C_{13}H_{17}ONS$	5.95 5.89	5.95	13.70 13.66	13.61
VIII		183-186 (7 mm) M.p. 59°	57	$C_{14}H_{17}ONS$	5.70 5.72	5.66	12.78 12.73	12.95
IX	$CH_2=CH-CH_2-$	151-152 (7 mm)	51	$C_{11}H_{11}ONS$	6.91 6.96	6.82	15.49 15.75	15.60

Under these conditions, p-tolylbenzylic ester forms benzaldehyde, 3,5-dinitro-4-oxy-methylbenzene and 4-nitrobenzyl nitrate [19]. The dibenzyl ester does not give a nitration product, but only the oxidation products, namely, benzaldehyde and benzoic acid [17].

Nitration of 2-alkoxymethylbenzthiazole was carried out in the author's work. Reacting the nitration mixture with 2-methoxymethyl- (I), 2-ethoxymethyl- (II), 2-propoxymethyl- (III) and 2-butoxymethyl- (V) -benzthiazoles, gave products in the molecules of which the nitro group occupied the 6 position. This fact was proved by oxidation of the resulting nitro derivatives to nitrobenzthiazole-2-carboxylic acid, and its decarboxylation to 6-nitrobenzthiazole.

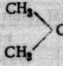
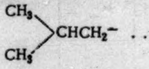
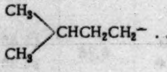
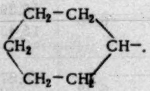
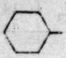
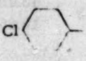
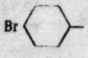
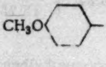
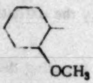
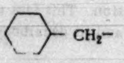
Nitration of 2-isopropoxymethyl-(IV), 2-isobutoxymethyl-(VI), 2-isoamyloxymethyl-(VII) and 2-allyloxymethyl-(IX)-benzthiazoles under the same conditions leads to formation of 2-oxymethyl-6-nitrobenzthiazole. Thus, along with the nitration process, there occurs desalkylation of the alkoxy group containing the branched chain of carbon atoms, or the multiple bond.

Similar weakening of stability in the branched alkyl bond with ester oxygen was observed by Tronov and Ladygina [20], during hydrolysis of the alkyl esters of phenol with hydrobromic acid.

Upon nitration of the indicated 2-alkoxymethylbenzthiazoles, containing branched alkyl or allyl radicals, 2-benzthiazolylaldehyde was isolated from acetic anhydride medium, i.e., under these conditions, nitration does not proceed at all, but oxidation of the alkoxymethyl group to the aldehyde group occurs. As was indicated above, a similar phenomenon is observed upon nitrating isobutyl- and isoamylbenzyl esters, as well as by nitrating the dibenzyl ester.

TABLE 3

Chloroanhydrides of Alkoxy- and Aryloxyacetic Acids of the General Formula $ROCH_2COCl$

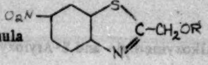
Preparation Number	R	Boiling point		Yield (%)	Literature
		author's data	literature data		
I		127-129°	139-141°	87	[21]
II		59 (25 mm)	59 (25 mm)	67	[3]
III	 . . .	57-62 (8 mm)	–	69	–
IV	$n\text{-}C_8H_{17}-$	125-126 (12 mm)	125-126 (12 mm)	72	[5]
V		105 (20 mm)	115-117 (30 mm)	74	[7]
VI	$CH_2{=}CH-CH_2-$	48-50 (12 mm)	–	75	–
VII		225-226	225-226	78	[9]
VIII		135-136 (15 mm)	142 (17 mm)	93	[10]
IX		154 (12 mm)	–	85	–
X		159-160 (20 mm)	–	86	–
XI		151 (20 mm)	–	80	–
XII		105-107 (5 mm)	81 (0.2 mm)	51	[13]

In connection with the interference encountered in nitration of 2-alkoxymethylbenzthiazoles with branched carbon chains, the author synthesized the corresponding 2-alkoxymethyl-, as well as the 2-aryloxymethyl-6-nitrobenzthiazoles, according to Scheme II, by condensing 5-nitro-2-aminophenylmercaptan with alkoxy and aryloxyacetic acid chloroanhydrides.

A large number of alkoxy- and aryloxyacetic acid chloroanhydrides are described in the literature, the remaining being synthesized by the author, for the first time; they were not analyzed, but were identified in the form of condensation products with 5-nitro-2-aminophenylmercaptan. The boiling points and yields of these chloroanhydrides are given in Table 3.

5-Nitro-2-aminophenylmercaptan has received but little study. It was obtained for the first time by Mylius by splitting 6-nitrobenzthiazole with alcoholic alkali [22], and then by Jacobson and Kwaysser by splitting 2-oxy-5-nitrobenzthiazole with aqueous ammonia in a sealed tube [23].

TABLE 4

2-Alkoxymethyl- and 2-Aryloxymethyl-6-nitrobenzthiazoles of the General Formula 

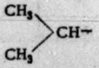
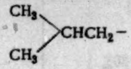
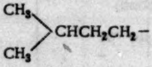
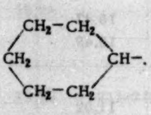
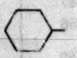
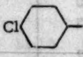
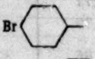
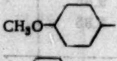
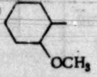
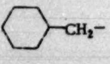
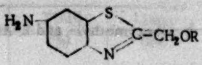
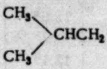
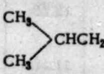
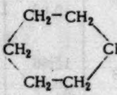
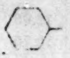
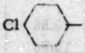
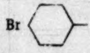
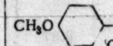
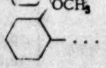
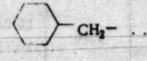
Preparation Number	R	Melting point	Yield (%)	Empirical formula	Analytical results			
					nitrogen (%)		sulfur (%)	
					found	calc'd	found	calc'd
I	CH_3-	137-138°	64	$C_9H_8O_3N_2S$	12.45 12.44	12.50	14.38 14.39	14.28
II	CH_3CH_2-	111.5	70	$C_{10}H_{10}O_3N_2S$	11.48 11.56	11.76	12.96 12.87	13.44
III	$CH_3CH_2CH_2-$	72	35	$C_{11}H_{12}O_3N_2S$	11.22 11.30	11.11	12.74 12.67	12.69
IV	 $(CH_3)_2CH-$	101.4	25	$C_{11}H_{12}O_3N_2S$	10.90 10.98	11.11	12.66 12.60	12.69
V	$CH_3CH_2CH_2CH_2-$	83-84	66	$C_{12}H_{14}O_3N_2S$	10.67 10.75	10.52	12.19 12.38	12.02
VI	 $(CH_3)_2CHCH_2-$	86	58	$C_{12}H_{14}O_3N_2S$	10.52 10.56	10.77	12.17 12.28	12.30
VII	 $(CH_3)_2CHCH_2CH_2-$	63	25	$C_{13}H_{16}O_3N_2S$	10.08 9.89	10.00	11.52 11.51	11.42
VIII	n-$C_8H_{17}-$	69	45	$C_{16}H_{22}O_3N_2S$	8.65 8.78	8.69	10.05 10.03	9.93
IX		96-97	58	$C_{14}H_{16}O_3N_2S$	9.44 9.28	9.58	10.68 10.71	10.95
X	$CH_2=CH-CH_2-$	69	41	$C_{11}H_{10}O_3N_2S$	11.17 11.10	11.20	12.66 12.70	12.80
XI		161-162	84	$C_{14}H_{10}O_3N_2S$	9.60 9.50	9.79	10.86 10.96	11.18
XII		153-154	80	$C_{14}H_9O_3N_2SCl$	8.62	8.73	–	–
XIII		167-168	86	$C_{14}H_9O_3N_2SBr$	7.69 7.71	7.67	8.97	8.76
XIV		144-145	82	$C_{15}H_{12}O_4N_2S$	8.88 8.72	8.86	10.02 10.09	10.12
XV		120-121	51	$C_{15}H_{12}O_4N_2S$	8.90 8.72	8.86	10.24 10.11	10.12
XVI		75-76	70	$C_{15}H_{12}O_3N_2S$	9.13 9.09	9.33	10.78 10.55	10.66

TABLE 5

2-Alkoxymethyl- and 2-Aryloxymethyl-6-aminobenzthiazoles of the General Formula 

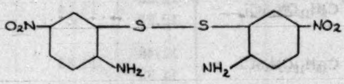
Preparation Number	R	Base			Analytical	
		Melting point	Yield (%)	Empirical formula	nitrogen (%) found	nitrogen (%) calculated
I	CH_3–	–	–	–	–	–
II	CH_3CH_2–.	–	–	–	–	–
III	$CH_3CH_2CH_2$–	–	–	–	–	–
IV	$CH_3CH_2CH_2CH_2$–.	–	–	–	–	–
V	 $(CH_3)_2CHCH_2$–.	–	–	–	–	–
VI	 $(CH_3)_2CHCH_2CH_2$–	–	–	–	–	–
VII	n-C_8H_{17}–	–	–	–	–	–
VIII		108*	68	$C_{14}H_{18}ON_2S$	10.47 10.49	10.67
IX		147-148	50	$C_{14}H_{12}ON_2S$	11.02 11.10	10.94
X		173	75	$C_{14}H_{11}ON_2SCl$	9.47 9.56	9.62
XI		181-182.5	83	$C_{14}H_{11}ON_2SBr$	8.50 8.53	8.36
XII		148	88	$C_{15}H_{14}O_2N_2S$	9.77 9.79	9.79
XIII		157.5	72	$C_{15}H_{14}O_2N_2S$	9.86 9.85	9.79
XIV	 . . .	–	–	–	–	–

Base		Hydrochloride					
results				Analytical results			
sulfur (%)		Melting point	Empirical formula	nitrogen (%)		chlorine (%)	
found	calculated			found	calculated	found	calculated
–	–	247* (decomp)	$C_9H_{11}ON_2SCl$	12.33 12.23	12.14	15.44 15.49	15.40
–	–	215 (decomp)	$C_{10}H_{13}ON_2SCl$	11.48 11.32	11.45	14.55	14.53
–	–	208-210 (decomp)	$C_{11}H_{15}ON_2SCl$	10.90 10.79	10.83	13.56 13.59	13.73
–	–	204 (decomp)	$C_{12}H_{17}ON_2SCl$	10.23 10.40	10.27	Sulfur 11.89	11.74
–	–	206-207 (decomp)	$C_{12}H_{17}ON_2SCl$	10.69 10.56	10.27	–	–
–	–	208-209 (decomp)	$C_{13}H_{19}ON_2SCl$	9.36 9.58	9.77	–	–
–	–	187 (decomp)	$C_{16}H_{25}ON_2SCl$	8.60 8.49	8.52	10.76 10.90	10.80
11.93 11.97	12.21	–		–	–		
12.37 12.28	12.50	211-212	$C_{14}H_{13}ON_2SCl$	9.63 9.66	9.57	12.04 12.06	12.13
	–	231-232	$C_{14}H_{12}ON_2SCl_2$	8.78 8.67	8.56	21.46	21.71
Bromine 23.83 24.01	23.88	238-238.5	$C_{14}H_{12}ON_2SClBr$	7.36 7.48	7.53	–	–
11.08 11.19	11.19	217 (decomp)	$C_{15}H_{14}ON_2SCl$	8.96	8.68	10.69 10.65	11.00
11.00 11.05	11.19	189	$C_{15}H_{14}O_2N_2SCl$	8.07	8.68		
–	–	207-208 (decomp)	$C_{15}H_{15}ON_2SCl$	9.17 9.30	9.13	11.65 11.72	11.61

The author obtained 5-nitro-2-aminophenylmercaptan in 83% yield by heating 2-oxy-6-nitrobenzthiazole with aqueous ammonia in an autoclave. The m.p. was 89-90° (Jacobson and Kwaysser indicated a yield of about 60%. m.p. 83-84°).

To identify the 5-nitro-2-aminophenylmercaptan obtained by the author, it was condensed with formic acid. The product with m.p. 176-177° was isolated in quantitative yield, which did not produce depression in a mixed sample with 6-nitrobenzthiazole obtained by nitration of benzthiazole. A product with m.p. 164° was isolated by condensation with acetyl chloride, and gave no depression in a mixed sample with 2-methyl-6-nitrobenzthiazole, obtained by nitration of 2-methylbenzthiazole.

Attempts to carry out condensation of 5-nitro-2-aminophenylmercaptan with alkoxy- and aryloxy-acetic acids by heating the components in benzene or toluene did not lead to positive results. Each time a disulfide separated with a m.p. of 237-238°:



synthesized for the first time by Jacobson and Kwaysser by oxidation of 5-nitro-2-aminophenylmercaptan. Its formation as a result of heating with alkoxy and aryloxyacetic acids is an indication of its tendency to auto-oxidation.

It was found that 2-alkoxymethyl-6-nitrobenzthiazoles are formed very readily at room temperature, by interacting 5-nitro-2-aminophenylmercaptan with chloranhydrides of alkoxyacetic acids. In these reactions, disulfide is found to be only a side product.

Upon interacting 5-nitro-2-aminophenylmercaptan with the chloroanhydride of aryloxyacetic acids in pyridine. or without solvent, products are formed, whose analysis corresponds to the diacyl derivatives of 5-nitro-2-aminophenylmercaptan.

After arranging condensation experiments in the presence of anhydrous zinc chloride, reaction went in the desired direction. and a series of 2-aryloxy-6-nitrobenzthiazoles was obtained.

New bases, resulting from condensation of 5-nitro-2-aminophenylmercaptans with alkoxy- and aryloxyacetic acid chloroanhydrides, are given in Table 4. Preparations I, II, III, and IV were obtained by nitration of the corresponding 2-alkoxymethylbenzthiazoles. 2-Alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles, were in the form of light yellow crystals, soluble in organic solvents, wherein the 2-aryloxy derivatives are much less soluble than the 2-alkoxymethyl-6-nitrobenzthiazoles.

Reduction of these nitro derivatives was carried out with iron shavings in a water-alcohol medium, in the presence of a small amount of acetic acid.

2-Alkoxymethyl-6-aminobenzthiazoles are liquids. They were identified as their hydrochlorides. Acetyl derivatives were obtained for some of them. The 2-aryloxymethyl-6-aminobenzthiazoles are well-crystallizing compounds, with boiling points above 100°. Yields, melting points, and analyses for the isolated amines are given in Table 5.

The amines were converted into the corresponding hydrochlorides and acetal derivatives. Analyses and melting points of the 2-alkoxymethyl- and 2-aryloxymethyl-6-aminobenzthiazole hydrochlorides are given in Table 5. The salts are in the form of colorless crystals. The 2-alkoxymethyl-6-aminobenzthiazole hydrochlorides are readily soluble in water, alcohol and acetone; the aryloxymethyl-5-aminobenzthiazole hydrochlorides are very poorly soluble in water, and in alcohol, they dissolve with greater difficulty than with the alkoxy salt derivative.

2-Alkoxymethyl-6-aminobenzthiazole hydrochlorides, in contrast to the 2-alkoxy-6-aminobenzthiazole hydrochlorides [2], are found to be stable compounds. The author did not observe noticeable desalkylation when synthesizing them.

The acetyl derivatives of 2-alkoxymethyl- and 2-aryloxymethyl-6-aminobenzthiazoles are given in Table 6. They are in the form of colorless crystals. 2-Alkoxymethyl-6-aminobenzthiazoles, when treated with acetic anhydride, give liquid products which are evidently mixtures, and therefore in only two cases was it possible to isolate pure crystalline acetyl derivatives. 2-Aryloxymethyl-6-aminobenzthiazoles form readily crystallizing substances, and were recrystallized from benzene.

EXPERIMENTAL

o-Aminophenylmercaptan. Obtained from Captax, according to the method developed by Kiprianov and Ushenko [24].

Alkoxyacetic Acids. (See Table 1). Prepared by boiling solutions of the alcoholates in the corresponding alcohols, with a small excess of chloroacetic acid.

Aryloxyacetic Acids. (See Table 1). Prepared by boiling the corresponding phenols with chloroacetic acid in the calculated amount of 10% sodium hydroxide solution.

Alkoxy- and Aryloxyacetic Acid Chloroanhydrides (See Table 3). Obtained by heating the acids with 15% excess of thionyl chloride on a water bath at 60° for 2 hours. After distilling off the thionyl chloride excess, the chloroanhydrides were distilled in vacuo.

Jacobson and Kwaysser obtained 5-nitro-2-aminophenylmercaptan, starting from phenyl mustard oil, which was converted via the urethane into 2-oxybenzthiazole.

The author obtained 2-oxybenzthiazole from Captax in very good yield according to the method proposed by Efros and Davidenkov [25].

2-Oxy-6-nitrobenzthiazole was prepared as follows: 45 ml of nitric acid (d 1.38) in 45 ml of concentrated sulfuric acid mixture was introduced dropwise, and with mechanical stirring at 5 - 10°, was slowly added to a solution of 60.4 g (0.4 mole) of 2-oxybenzthiazole in 100 ml of concentrated sulfuric acid. The nitrating mixture was added over a period of 45 minutes, and after completion of addition of the mixture, the reaction mass was stirred for 30 minutes at room temperature, and then poured onto chipped ice. The resulting precipitate was filtered off, washed several times with water, dried, and recrystallized from glacial acetic acid. The m.p. was 248°, yield of recrystallized product being 42 g (54%).

A suspension of 59 g of 2-oxy-6-nitrobenzthiazole in 750 ml of ammonia (d 0.950) was heated in an autoclave with a stirrer at 150° for 4 hours. After cooling, the resulting dark-red, ammoniacal solution was filtered, the filtrate neutralized with dilute hydrochloric acid, with external cooling. The resulting light-yellow precipitate was filtered off, washed with water, thoroughly pressed out, and dried in a vacuum desiccator over sulfuric acid. The m.p. was 84 - 85°, yield 42.3 g (83%). After recrystallization from aqueous alcohol, the melting point of 5-nitro-2-aminophenylmercaptan was 89 - 90°.

2-Alkoxymethylbenzthiazoles. (Table 2).

A mixture of 10 g (0.08 mole) of o-aminophenylmercaptan and 0.1 mole of the corresponding alkoxyacetic acid was heated on an oil bath at 135 - 140° for 3 - 4 hours. After cooling, 5 ml of 10% sodium hydroxide was added and the oil which separated was extracted with ether. The ether solution was dried over anhydrous potash, and after distilling off the ether, it was distilled in vacuo.

Nitration of 2-Alkoxymethylbenzthiazoles.

5 ml of nitric acid (d 1.38) was added dropwise at 5 - 10°, with mechanical stirring, for a period of 30 minutes, to a solution of 5.7 g of 2-methoxymethylbenzthiazole in 25 ml of concentrated sulfuric acid. After stirring for 1 hour at room temperature, the reaction mass was poured into ice water. The resulting precipitate was filtered, washed with water, dried, and recrystallized from alcohol. Preparations II, III and V (Table 4) were similarly prepared.

Determination of the Nitro Group Position in Nitration Products of 2-Alkoxymethylbenzthiazoles. 1) 5% potassium permanganate (30 ml) and 5 ml of 5% sodium hydroxide were added to 0.5 g of 2-alkoxymethylbenzthiazole nitroderivative, and the mixture boiled for 1 hour. After filtration of the reaction mixture, the filtrate was decolorized with a small amount of perhydrol, again filtered, and neutralized with dilute hydrochloric acid. A precipitate with m.p. 174° separated from the solution, and did not give depression when mixed with a sample of 6-nitrobenzthiazole, obtained by nitration of benzthiazole.

2) Upon nitrating 2-isopropoxymethyl-, 2-isobutoxymethyl-, 2-isoamyloxymethyl- and 2-allyloxymethylbenzthiazoles under the same conditions, as were used for nitration of 2-alkoxymethylbenzthiazoles with a normal chain of carbon atoms, the precipitate which resulted in all cases possessed one and the same m.p. of 167-168°. Analysis of this product for nitrogen indicated that it corresponded to 2-oxymethylnitrobenzthiazole.

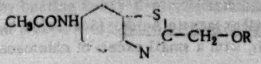
Found %: N 13.18, 13.01. $C_8H_6O_3N_2S$. Calculated %: N 13.33.

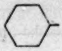
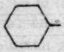
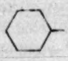
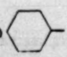
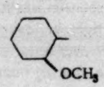
Determination of the melting point on a mixed sample with 2-oxymethyl-6-nitrobenzthiazole, obtained according to Zubarovsky by nitration of 2-oxymethylbenzthiazole, did not produce depression.

3) 2.35 g of isoamyloxybenzthiazole in 8 ml of acetic anhydride was added with stirring, at room temperature, to a solution of 1 ml of nitric acid (d 1.5) in 15 ml of glacial acetic acid. Having completed addition of

TABLE 6

Acetyl Derivatives of 2-Alkoxymethyl- and 2-Aryloxymethyl-6-aminobenzthiazole of the General Forumla:



Prep-aration No.	R	Melting point	Empirical formula	Analytical results			
				Nitrogen (%)		Sulfur (%)	
				Found	Calc'd	Found	Calc'd
I	CH_3CH_2-	108 - 109°	$C_{12}H_{14}O_2N_2S$	11.10 11.02	11.20	12.68 12.74	12.80
II	$CH_3CH_2CH_2CH_2-$	92 - 93	$C_{14}H_{18}O_2N_2S$	10.06 10.26	10.07	11.47 11.56	11.51
III		160	$C_{16}H_{14}O_2N_2S$	9.25 9.16	9.39	10.63 10.56	10.73
						Chlorine	
IV	Cl 	200	$C_{16}H_{13}O_2N_2SCl$	8.49 8.42	8.42	10.66 10.74	10.68
V	Br 	199	$C_{16}H_{13}O_2N_2SBr$	7.53 7.36	7.45	–	–
VI	CH_3O 	166	$C_{17}H_{16}O_3N_2S$	8.28 8.35	8.53	–	–
VII		145	$C_{17}H_{16}O_3N_2S$	8.44 8.49	8.53	–	–

thiazole, the reaction mixture was heated for 15 minutes at 50° and was left for 1 hour at room temperature. Upon pouring into ice water, a yellow oil precipitated, which was extracted with ether. The ether solution was dried with sodium sulfate, and after distilling off the ether, the residue was distilled in vacuo at 6 mm and 100 - 135°. The major portion of distillate solidified and was recrystallized from petroleum ether. M.p. 74°. Analysis for nitrogen and sulfur corresponded to benzthiazolylaldehyde, and not to the expected 2-isoamyloxymethyl-6-nitrobenzthiazole.

Found %: N 8.62, 8.46; S 19.77, 19.72. C_8H_5ONS. Calculated %: N 8.58; S 19.73.

Determination of the melting point of a sample mixed with 2-benzthiazolylaldehyde* did not give depression.

Nitrationof 2-isopropoxymethyl-, 2-isobutoxymethyl-, and 2-isoallyloxymethylbenzthiazoles led to the same results under conditions indicated above, i.e.,with formation of 2-benzthiazolylaldehyde in 30 - 35% yield.

Condensation of 5-Nitro-2-aminophenylmercaptan with Alkoxyacetic Acid Chloroanhydrides.

3.4 g (0.02 mole) of 5-nitro-2-aminophenylmercaptan was ground throughly with 0.021 mole (slight excess) of alkoxyacetic acid chloroanhydride. Spontaneous evolution of heat was observed, and the yellow color of 5-nitro-2-aminophenylmercaptan changed to orange. The mixture was left standing for 10 minutes, and was then suspended in 20 ml of 5% sodium hydroxide solution. The precipitate was filtered off, washed with water, and after drying in air, was recrystallized from dilute alcohol. Preparations IV, VI, VII, VIII and IX (Table 4) were obtained in similar fashion.

Formation of a substance, poorly soluble in alcohol, was observed as a side product of the reaction. After crystallization fom glacial acetic acid, the substance melted at 237 - 238°. This melting point corresponded to the melting point of the disulfide. Analysis for nitrogen confirmed this assumption.

Found %: N 16.40. $C_{12}H_{10}O_4N_4S_2$. Calculated %: N 16.57.

Condensation of 5-Nitro-2-aminophenylmercaptan with Aryloxyacetic Acid Chloroanhydrides.

1) 1.7 g (0.01 mole) of 5-nitro-2-aminophenylmercaptan was ground thoroughly with the chloroanhydrides (0.012 mole) of phenoxyacetic, p-chlorophenoxyacetic and o-methoxyphenoxyacetic acids; spontaneous evolution

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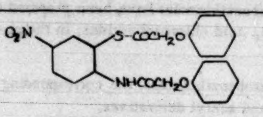
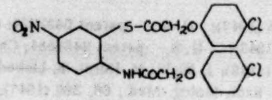
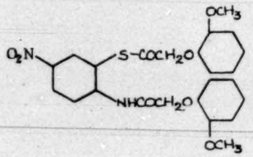
* 2-Benzthiazolylaldehyde was kindly furnished to us by V. M. Zubrovsky.

of heat was observed, evolution of hydrogen chloride, and a change in color of 5-nitro-2-aminophenylmercaptan. After standing for some time, the reaction mixture was suspended in 20 ml of 5% sodium hydroxide solution, the precipitate filtered off, washed with water, and after drying, was recrystallized from acetic acid, since the precipitate was insoluble in alcohol. Analyses of the synthesized preparations corresponded to the acylation products, whose assumed structure is given in Table 7.

2) 3.4 g (0.02 mole) of 5-nitro-2-aminophenylmercaptan was suspended in dry ether, and 0.022 mole of aryloxyacetic acid chloroanhydride solution in ether and 3 g of anhydrous zinc chloride, added to the suspension; boiling up of the reaction mixture and conversion to a red color was observed. The reaction mixture was then boiled gently on a water bath for 30 minutes, the ether distilled off, the residue suspended in water, filtered, washed with 5% sodium hydroxide solution, and then water. After drying, the precipitate of 2-aryloxymethyl-6-nitrobenzthiazole was recrystallized from glacial acetic acid. The preparations obtained in this manner are given in Table 4 (XI-XVI).

TABLE 7

Prep. No.	Structure	Melting point	Empirical formula	Nitrogen (in %) Found	Nitrogen (in %) Calc'd	Sulfur (in %) Found	Sulfur (in %) Calc'd
I		173-174°	$C_{22}H_{18}O_6N_2S$	6.35 6.60	6.39 –	7.21 7.25	7.30 –
						Chlorine	
II		204	$C_{22}H_{16}O_6N_2SCl_2$	5.38 5.34	5.52 –	13.85 13.97	14.00 –
III		149-150	$C_{24}H_{22}O_8N_2S$	5.96 6.06	5.62 –	–	–

2-Alkoxymethyl- and 2-Aryloxymethyl-6-aminobenzthiazoles (Table 5).

15 g of iron shavings and 10 ml of 20% acetic acid were added to a boiling solution of 0.015 mole of 2-alkoxymethyl- or 2-aryloxymethyl-6-nitrobenzthiazole in 50 ml of alcohol (in the case of poorly-soluble nitro-compounds, a suspension was used). The mixture was boiled on a water bath for 1 hour stirring, and 20 ml of water added in portions, over this period of time. Boiling on a water bath was continued for another hour, and the reaction mixture was then filtered. The filtrate was diluted with water. In those cases where an oily product separated upon dilution with water, the product was extracted with ether, dried with anhydrous sodium sulfate, and after distilling off the ether, the remaining amine identified in the form of its hydrochloride and acetyl derivatives. In those cases where the amine precipitated in the form of a crystalline precipitate, it was filtered and recrystallized from dilute alcohol. The amines were converted into the hydrochlorides when their alcoholic solutions were combined with the ether solution of hydrogen chloride. Recrystallized from alcohol by addition of a small amount of ether.

The acetyl derivatives were obtained by short boiling of the amine with acetic anhydride (Table 6).

SUMMARY

1. A number of 2-alkoxymethylbenzthiazoles have been obtained.

2. 2-Alkoxymethyl-6-nitrobenzthiazoles are formed upon nitrating 2-alkoxymethylbenzthiazoles containing an alkyl group with the normal chain of carbon atoms.

3. Upon nitrating 2-alkoxymethylbenzthiazoles containing an alkyl with branched chain carbon atoms, or a short chain, with a mixture of nitric and sulfuric acids, simultaneous desalkylation occurs along with the nitration process. 2-Oxy-6-nitrobenzthiazole is formed.

4. Upon nitrating the same alkoxymethylbenzthiazoles in acetic anhydride medium, the alkoxymethyl group oxidizes to an aldehyde group, and 2-benzthiazolylaldehyde is formed.

5. Diacyl derivatives are formed upon interaction of 5-nitro-2-aminophenylmercaptans with the chloroanhydrides of aryloxyacetic acids in the absence of zinc chloride.

6. A number of 2-alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles have been prepared by condensing 5-nitro-2-aminophenylmercaptan with alkoxy- and aryloxyacetic acid chloroanhydrides, in the presence of anhydrous zinc chloride.

7. Upon reducing 2-alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles, the corresponding amines have been prepared, which have been converted into the hydrochloride and acetyl derivatives.

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* See Consultants Bureau Translation, page 2331.

DIRECT IODINATION OF BENZENE, TOLUENE, CHLOROBENZENE, IODOBENZENE AND p-NITROTOLUENE

A. N. Novikov

Upon halogenating benzene with elementary iodine in the presence of nitric acid (d 1.5) [1], nitro compounds result in addition to the main reaction product of iodobenzene. The recommended method for purifying by reduction does not give satisfactory results. The iodobenzene which results in practice contains traces of nitrobenzene. Duration of the process, and the use of nitric acid of specific gravity 1.5 can also be included among shortcomings of this process.

Directions are also found in the literature for the use of other relatively ineffective oxidants in the iodination of benzene [2]. Recently, a synthetic method for producing iodobenzene from benzene and iodine in the presence of relatively costly materials such as the silver salts of perchloric acid [3], of sulfuric acid [4] and of trifluoroacetic acid [5] have been described in the literature. Despite this fact, iodobenzene is synthesized chiefly from aniline and not by direct iodination of benzene.

Tronov and Novikov [6] synthesized m-iodobenzoic acid and m-iodobenzaldehyde by direct iodination of benzoic acid and benzaldehyde in the presence of a standard nitrating mixture.

It was of considerable interest to test a sulfuric-nitric mixture upon iodination reactions of benzene and other aromatic compounds.

As a result of arranging experiments, iodobenzene, a mixture of o- and p-iodotoluenes, p-diiodobenzene, p-iodochlorobenzene and 2-iodo-4-nitrotoluene were prepared free from nitro compound impurities.

EXPERIMENTAL*

Iodination of Benzene. A pre-cooled mixture, preared in advance, composed of glacial acetic acid (20 ml) and sulfuric acid (5.5 ml) was placed in a three-necked round-bottomed flask containing iodine (6.35 g) and benzene (7 ml). 1.6 ml of nitric acid (d 1.4) was gradually added, with vigorous mechanical stirring, to the reaction vessel, 46°, over a period of 45 minutes, from a buret. Heating was continued for another 15 minutes. The color of the reaction mixture was dark-brown.

The mixture was diluted with water, the resulting heavy oily liquid separated from the aqueous acid layer, washed free of acids, treated with sodium sulfite and water. The oil was fractionated after being dried over calcium chloride. Benzene in unchanged form distilled off first, and then at 186 - 187.5°, iodobenzene distilled off. A small residue crystallized out in the distilling flask upon cooling (apparently diiodobenzene). The yield of iodobenzene was 80 % (8.0 g) on the basis of iodine taken for reaction.

Found (according to Stepanov) %: I 63.0. C_6H_5I. Calculated %: I 62.3.

Test for nitrogen after decomposition with sodium was negative. Treatment with stannous chloride and hydrochloric acid, with subsequent addition of sodium nitrite and β-naphthol did not produce a colored solution, indicating absence of the nitro group.

An increase in the amount of nitric acid, a decrease in the amount of glacial acetic acid, and an increase in the reaction temperature, promote formation of nitrobenzene. Slow stirring, or the absence of sulfuric acid, lower considerably the yield of product. Addition of a small amount of urea (0.3 - 0.5g) made it possible to carry out the reaction without withdrawal or trapping of nitrogen oxides.

Iodination of Toluene. A mixture of 8.5 ml of toluene, 6.35 g of iodine, 5.5 ml of sulfuric acid, and 20 ml of glacial acetic acid was heated at 45°. 1.3 ml of nitric acid was introduced into the flask with vigorous stirring, over a period of 35 minutes. Reaction time was 4 minutes. The oily reaction product, after drying, was distilled under standard conditions. At 207-212° 9.4 g (95 %) of o- and p-iodotoluene mixture was collected. A second distillationgave two fractions: 1st fraction – b.p. 205-209°, 1.5 g; 2nd fraction – b.p. 209-210°, 7.8 g (70 %). Upon oxidizing the 2nd fraction with dilute nitric acid at 135°, p-iodobenzoic acid resulted with m.p. 269°. Qualitative test for nitrogen was negative.

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* V.A. Sensky, P. F. Koronin, B. F. Lagerev, A. N. Polyakova, and K. S. Savelyeva participated in the experimental portion of this work.

Found (according to Stepanov) %: I 58.4. C_7H_7I. Calculated %: I 58.2.

Iodination of Benzene. Nitric acid (2.7 ml0 was added with mechanical stirring over a period of 25 minutes to a mixture of 5.6 ml of iodobenzene, 6.35 g of iodine, 5.6 ml of sulfuric acid, 30 ml of glacial acetic acid and 4 ml of carbon tetrachloride at 115°. Reaction lasted for 35 minutes. The reaction mixture was diluted with water, and solid diiodobenzene separated, was washed with water and alcohol (5 ml). The yield was 8.9 g (55%). M.p. was 130-131° (from ethanol). 4 g of oil (20%) remained in the residue. This was apparently o-diiodobenzene.

Found (according to Stepanov) %: I 76.4. $C_6H_4I_2$. Calculated %: I 76.9.

Iodination of Chlorobenzene. Carried out under the same conditions as for iodobenzene. p-Chloroiodobenzene resulted in 40% yield. M.p. was 55-56°. The o-isomer was detected in the form of an oil.

Iodination of p-Nitrotoluene. 6.85 g of nitrotoluene, 6.35 g of iodine, 11.2 ml of sulfuric acid, 3.4 ml of nitric acid, 6 ml of carbon tetrachloride and 15 ml of glacial acetic acid. Temperature of the reaction was 100°, time 3 hours. The nitric acid was added uniformly over a period of 35 minutes. After reaction the mixture was distilled with steam, and the unreacted iodine and p-nitrotoluene removed. The yield of iodonitrotoluene was 70 %, m.p. 58° (from methanol).

Found (according to Stepanov) %: I 47.1. $C_7H_6NO_2I$. Calculated %: I 48.2.

SUMMARY

1. Sulfuric-nitric acid mixture can be used successfully for the iodination reaction of many aromatic compounds.

2. By carrying out a direct iodination under strictly specified conditions, and without excess of nitric acid, iodo derivatives without contaminating nitro compounds can be prepared.

3. There have been prepared by direct iodination reaction in the presence of nitrating mixture: iodobenzene, p-diiodobenzene, a mixture of o- and p-iodotoluenes, p-chloroiodobenzene and 2-iodo-4-nitrotoluene.

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CATALYTIC CONVERSION OF HALOGEN DERIVATIVES IN THE AROMATIC SERIES

I. ISOMERISM OF THE MONOCHLORONAPHTHALENES

N. N. Vorozhtsov, Jr., and A. M. Beskin*

The isomerization reaction for halogen compounds of the aliphatic series was described back in 1875 by Eltekov [1], and later by Favorsky [2], who studied it with considerable thoroughness.

Possibility of isomerization was also demonstrated for some halogen derivatives of the aromatic series; however, no one has, as yet, succeeded in obtaining satisfactory yields of isomerization products, in particular as regards the most interesting halogen derivatives.

Thus, Roux [3], for the first time succeeded in isomerizing 1-bromo- and 1-chloronaphthalenes by reacting these substances with aluminum chloride in carbon disulfide. 2-Bromo- and 2-chloro-naphthalenes, respectively, were isolated in small amounts from the reaction mass, as well as naphthalene and dihalogen derivatives, in addition to the initial monohalogen compound of naphthalene.

Fischer and Clark [4] demonstrated later that when certain metals (Sb, Mo, Ni, W, Cr) are added to aluminum chloride, the yield of 2-bromonaphthalene can be increased to 25% (yield being 9.1% without these additives).

Meyer and Schiffner [5] isolated about 1% of not very pure 2-bromonaphthalene by passing vapors of 1-bromonaphthalene over silica gel.

Wibaut and coworkers [6] established that isomerization of 1-bromonaphthalene occurs upon heating it with ferric chloride in a stream of hydrogen bromide at 150°. The resulting mixture contained 60% 2-bromonaphthalene and 40% 1-bromonaphthalene. Noticeable quantitites of naphthalene and dibromonaphthalene were formed simultaneously. It was established that the isomerization reaction is reversible; a mixture of the same composition was obtained from 2-bromonaphthalene. Similar results were obtained by passing vapors of bromonaphthalene and hydrogen bromide over ferric chloride placed in pumice. In the opinion of the Dutch investigators, isomerization is effected by reversibility of the bromination process.

As is known, 1-chloronaphthalene is predominantly formed upon chlorination of naphthalene in the liquid phase, and about 10% 2-chloronaphthalene [7] is also present. Wibaut and Bloem [8] have recently demonstrated that when chlorination of naphthalene is carried out at a temperature above 350°, there is formed a mixture of monochloronaphthalenes, containing almost 50% of 2-chloronaphthalene. The yield of chloronaphthalenes mixture in this case is not very high (less than 50% of the naphthalene entering into reaction).

The authors have investigated the synthesis of 2-chloronaphthalene by the method of catalytic vapor phase isomerization of 1-chloronaphthalene.

Testing of various catalysts has indicated that at 400° chloronaphthalene does not change noticeably when passed with a stream of hydrogen chloride over silica gel and phosphoric acid on kieselguhr. At the same time, use of synthetic aluminosilicate catalyst and aluminum oxide under the same conditions leads to considerable isomerization of 1-chloronaphthalene. The catalyzate which resulted consisted of a mixture of 1- and 2-chloronaphthalenes, containing about 50% of 2-chloronaphthalene. It was established that the presence of hydrogen chloride has a pronounced influence upon the isomerization process. Thus, on aluminum oxide, in a stream of carbon dioxide, isomerization does not occur at all.

Upon passing chloronaphthalene over aluminosilicate catalyst, isomerization proceeds in a stream of carbon dioxide, and without any gas at all. However, with hydrogen chloride, the catalyst rapidly (after 15-30 minutes) decreases in activity. In the presence of hydrogen chloride, however, isomerization can be carried on for 2-3 hours (see Figure).

Decrease in catalyst activity is related to the accumulation of high-molecular-weight chloronaphthalene decomposition products, formed as by-products, upon the catalyst. After 15 minutes of work, the catalyst contains about 2 - 2.5% carbon. The process of formation of these by-products apparently occurs with splitting off of hydrogen chloride, since the catalyzate possessed some (up to 0.04 - 0.08%) HCl, and the C:Cl ratio accumulating on the catalyst is higher than in the initial chloronaphthalene.

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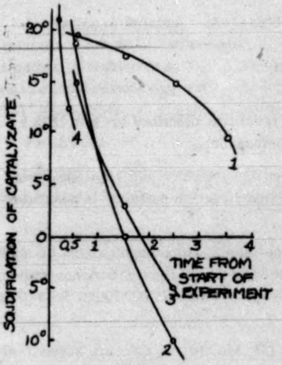
* Deceased.



Modification of the Extent of Isomerization with Respect to Duration of Catalyst Activity.

1) In a stream of HCl; 2) in a stream of CO_2; 3) and 4) without gas: a) solidification temperature of catalyzate; b) time from start of experiment.

The favorable effect of hydrogen chloride upon the stability of the catalyst is apparently explainable by the fact that a high concentration of hydrogen chloride inhibits the pyrolysis process because of the fact that one stage of the process occurring with rupture of hydrogen chloride is reversible. The effect of hydrogen chloride on the catalyst for the given case is apparently identical with the effect of hydrogen, which ensures stability of catalyst in the aromatizing process; in this case the pyrolysis process occurs with cleavage of hydrogen [9].

Pyrolysis in the isomerization process for chloronaphthalene proceeds on a relatively small scale. The yield of catalyzate constitutes not less than 95% of the chloronaphthalene passed through. Activity of the catalyst can be completely regenerated by heating it in a stream of air.

Isomerization of 1-chloronaphthalene is a reversible process. This situation indicates first of all that repeated passage of catalyzate over catalyst does not lead to an increased yield of 2-chloronaphthalene. Reversibility was also proved by direct experiment: passage of 2-chloronaphthalene over aluminosilicate in a stream of hydrogen chloride at 350-400° gave a mixture of the 1- and 2-chloronaphthalenes, almost identical in composition to the one resulting from isomerization of 1-chloronaphthalene.

Investigation of 1-chloronaphthalene isomerization on aluminum oxide in a stream of hydrogen chloride indicated that hydrogen chloride reacts to a certain degree with the catalyst, gradually increasing its activity. Best results are obtained by preliminary treatment of Al_2O_3 at 350° with hydrogen chloride for 1.5 hours. The catalyst treated in such manner retains its activity (when working with a stream of hydrogen chloride) for 7 hours; in this case about 5% carbon accumulates on it. Catalyst activity can be regenerated by treating it with air and hydrogen chloride.

The optimal reaction temperature was found to be 350°, and the optimal mole ratio of HCl to $C_{10}H_7Cl$ equal to 3:1. In this case the solidification temperature for catalyzate was 23.8° (corresponding to a content of about 55% of the 2-isomer). Per liter of catalyst, 300-350 g. of 1-chloronaphthalene can be passed through in 1 hour.

The mother liquor, after separation of 2-chloronaphthalene, can be repeatedly returned in the process, without lowering the yield of catalyzate or changing its composition. Thus, it is possible to convert almost completely the 1-chloronaphthalene into 2-chloronaphthalene. Catalytic isomerization of 1-chloronaphthalene has been found a convenient method for preparing what up to the present time has been an almost inaccessible 2-chloronaphthalene.

EXPERIMENTAL

1-Chloronaphthalene was prepared by chlorination of naphthalene in benzene with subsequent distillation or fractionation on a dephlegmator of technical chloronaphthalene (GOST 2660-44).* The fraction with b.p. 252-258° and d_4^{15} 1.1954 - 1.2001 was used for the investigation. By analysis according to the concentration method [7], it was determined that the product contained little naphthalene (up to 1%) and dichloronaphthalene (up to 2%). The content of 2-chloronaphthalene as determined by solidification temperature of the product with pure 2-chloronaphthalene, was equal (in accordance with the literature data [7]) to 10.5%.

The catalyst was placed in a vertical, fire-resistant glass tube (24 mm in diameter), heated by an electric oven. The layer of catalyst (height 12-24 cm, volume 40-80 ml), was between two layers of glass, the upper of which (18 cm length) served for evaporation of the chloronaphthalene which was fed from a buret. The side outlet of the T-tube which connected the buret with the tube, served to feed in the gas. The lower end of the catalyst tube was joined to the receiver for liquid reaction products.

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* All-Union State Standard.

As catalysts for the isomerization, silica gel, phosphoric acid on kieselguhr, aluminum oxide and synthetic aluminosilicate were tested.

Experiments were carried out at 400°, and with a supply of 3.8 - 3.9 g of chloronaphthalene and 120 ml of hydrogen chloride per hour per 80 ml of catalyst. Course of the conversion was followed by the change in solidification temperature of catalyzate (the initial chloronaphthalene did not freeze at −15°). Experimental results are given in Table 1.

TABLE 1

Experiment No.	Catalyst	1-Chloronaphthalene passed through (in g)	Wt. of catalyzate (in g)	Solidification temp. of cat.	Precipitate isolated upon cooling to −5°		Solidification temp. of mother liquor	2-Chloronaphthalene content in catalyzate (in %)
					Wt. (in g)	Melting point		
1	Aluminosilicate	20.5	16.40	+20°	3.9	46 - 47°	+9°	51.0
2	Aluminum oxide	20.0	16.80	+17	4.7	46 - 47	+5	48.5
3	Phosphoric acid on kieselguhr.	19.3	17.35	Does not freeze at −15°	0	–	–	–
4	Silica gel	20.0	18.30		0	–	–	–

After one recrystallization from alcohol of the precipitates isolated in Experiments 1 and 2, colorless, lustrous scales resulted, with m.p. 56-57°. M.p.'s of 56, 58, 60 and 61° [11] are indicated in the literature for 2-chloronaphthalene. A sample mixed with 2-chloronaphthalene prepared from 2-naphthylamine (m.p. 56-57°) melted at 56-57°.

Found %: C 73.74, 73.92; H 4.12, 4.12. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.34.

The boiling points of the mother liquors (245-260°) were close to the boiling point of original product, which indicated no noticeable disproportionation reactions. The mother liquors were apparently a mixture of 1- and 2-chloronaphthalenes and their composition can be determined by solidification curves for similar mixtures [7, 8].

Isomerization of 1-Chloronaphthalene in the Presence of Various Gases.

Comparative isomerization experiments on Al_2O_3 (80 ml) in the presence of hydrogen chloride and carbon dioxide at 350° were carried out. The rate of gas passage was 65 ml. per minute. The results are given in Table 2.

TABLE 2

Gas	Experiment time	Chloronaphthalene passed through (in g)	Solidification temperature of catalyzate	Content of 2-chloronaphthalene (in %)
Hydrogen chloride	5 hrs.	37.5	+ 21°	54
Carbon dioxide	4 hrs. 15 min.	15.1	Does not freeze at −15°	–

Hence, on aluminum oxide, the isomerization process for chloronaphthalene proceeds only in the presence of hydrogen chloride. In the presence of carbondioxide, despite a somewhat longer contact time, isomerization does not proceed.

The effects of various gases were studied in more detail when using the aluminosilicate catalyst. The nature of change in activity of the catalyst in the presence of various gases, and absence of gases, was determined by the change in solidification temperature of the catalyzate during the isomerization process. Experiments were carried out under the following conditions: temperature 400°; the volume of aluminosilicate catalyst was 40 ml, the feed of chloronaphthalene was 8 - 10 g per hour, HCl feed was 80 ml per minute, and the feed of carbon dioxide was 100 ml per minute. Experimental results are given in Table 3.

TABLE 3

Gas	Solidification temp. of the catalyzate, resulting within			
	1st hour	2nd hour	3rd hour	4th hour
Hydrogen chloride . . .	19.4°	17.8°	14.6°	9.2°
Carbon dioxide	18.5	0	− 10	
Without gas	14.6	3.2	− 5	

Table 3 indicates that the presence of hydrogen chloride is not required for isomerization of chloronaphthalene; it only slows down the deactivation process of the catalyst. Isomerization without gas (perhaps the most interesting one) can give good results with less work by the catalyst. Thus, at 400° and a feed rate of 21.6 g of chloromaphthalene per hour per 40 ml of catalyst for the first 15 minutes resulted in a solidification temperature up to +21°. Within the next 15 minutes, catalyzate solidification temperature of +15.6° resulted.

Catalyst which has lost its activity contains a considerable amount of chloronaphthalene decomposition products. For example, analysis of the catalyst which was worked for 15 minutes at 400° indicated a content of 2.07% carbon and 0.32% chlorine (in another sample, 2.49% C and 0.59% Cl). It is of interest to note that the C:Cl ratio in the product accumulating on the catalyst is greater (4.5 - 6.5:1) than for chloronaphthalene (3.4:1). Consequently, decomposition of chloronaphthalene which occurs as a side reaction should proceed with cleavage of hydrogen chloride. Actually, the hydrogen chloride content of catalyzate amounted to 0.04 - 0.08% (determination carried out by titration with 0.1 N sodium hydroxide of catalyzate mixed with water). Decreasing the isomerization temperature to 350° gave a decreased hydrogen chloride content of 0.01 - 0.03% in the catalyzate. The yield of catalyzate fluctuated from 95.0 to 96.5% for the chloronaphthalene passed through (at 400°).

Activity of the aluminosilicate catalyst can be regenerated by standard procedure — passage of air through it. For the case given, it was necessary to pass air through for approximately 3 hours, at a rate of 0.2 - 0.5 liter per minute (for 40 ml of catalyst) at a temperature increasing from 400 to 500°. Regeneration can be repeated many times: there was no lowering of catalyst activity observable after 40 regenerations.

Isomerization of chloronaphthalene on aluminosilicate catalyst is completely inhibited by ammonia introduced into the catalyst area. Thus the catalyzate obtained by passage of 4.2 g of 1-chloronaphthalene at 400° over 40 ml of catalyst for 15 minutes with a simultaneous passage rate of 30 ml per minute for ammonia, did not freeze at −15°.

Isomerization of 1-Chloronaphthalene on Aluminum Oxide in the Presence of a Stream of Hydrogen Chloride.

Effect of the isomerization temperature was determined during passage of 8 g per hour of chloronaphthalene on 50 ml of aluminum oxide and 70 - 80 ml per minute hydrogen chloride (mole ratio $C_{10}H_7Cl:HCl = 1:4$). The duration of each experiment was 5 hours (Table 4). With respect to the fact that optimal isomerization temperature is 330-350°, experiments were set up to study the effect of contact time on the extent of isomerization at 330°. A ratio of $C_{10}H_7Cl : HCl$ was maintained equal to 1:3. The amount of catalyst was 50.ml. . Experiment time was 5 hours (Table 5).

TABLE 4

Temperature of experiment	300°	330	350	400
Solidification temperature of catalyzate	10.0°	21.0	21.5	17.0
Content of 2-chloronaphthalene (in %)	42.5°	53.0	52.5	48.5

TABLE 5

1-chloronaphthalene feed (in g per hour)	10.0	13.0	16.2	18.0	20.0
Solidification temperature of catalyzate	18°	19	19	17.5	11

The effect of 1-chloronaphthalene and hydrogen chloride ratio was studied at 400°. The quantity of reactants fed, and the catalyst volume, were varied in order to maintain contact time constant. Experiment time was 3 hours. Conditions and experimental results are given in Table 6.

The optimal ratio was subsequently found to be 1:3.

A study of the dynamics of change in activity of aluminum oxide in the isomerization process indicated that a very important effect upon the character of this change is shown upon treating the catalyst with hydrogen chloride. There is given in Table 7 the effect of preliminary catalyst treatment with hydrogen chloride upon the activity at the experimental temperature of 350°. Feed amounted to 16.2 g of $C_{10}H_7Cl$ per hour. Mole ratio was $C_{10}H_7Cl:HCl = 1:3$.

TABLE 6

Quantity of catalyst	$C_{10}H_7Cl$ feed (in g/hour)	HCl feed (ml per minute)	Mole ratio of $C_{10}H_7Cl:HCl$	Solidification temperature of catalyzate
30	24	60	1:1	− 3°
37.5	7.8	36	1:2	+ 17
50	7.8	53	1:3	+ 20
80	7.8	95	1:5	+ 18
80	4.0	100	1:10	+ 17

TABLE 7

Catalyst treatment time with HCl	Solidification temperature of the catalyzate obtained, within						
	1st hour	2nd hour	3rd hour	4th hour	5th hour	6th hour	7th hour
Without treatment	− 15°	+ 12.8°	+17.2°	+ 17.4°	+ 14.2°	+ 14.0°	+13.4°
1,5 hours	+ 22.4	+ 21.8	+21.8	+ 21.2	+ 19.6	+ 18.2	+18.2

Decrease of aluminum oxide activity is related to its carbonization. Analysis of the aluminum oxide which was worked for 7 hours, indicated 5.58% carbon content. After regeneration under the above-indicated conditions, and treating with hydrogen chloride, the activity of aluminum oxide was regenerated again.

In connection with the fact that only up to 25% 2-chloronaphthalene in terms of catalyzate weight separated upon freezing the catalyzate, while over half of the 2-chloronaphthalene contained in the catalyzate remained in solution form with 1-chloronaphthalene, making it difficult to separate, it appeared an interesting step to increase yield by subjecting the mother liquor from 2-chloronaphthalene to direct isomerization again. As was to be expected, the isomerization processes in mother liquor (mixture of 2-chloronaphthalene with 1-chloronaphthalene containing for example 40% 2-chloronaphthalene) proceeded in a manner identical with that for fresh 1-chloronaphthalene. Solidification temperature for the catalyzate was the same (19 - 20° with 3 hours of work). Thus, by separating the 2-chloronaphthalene crystallizing out and returning the mother liquor to the process, it is possible to convert almost all of the 1-chloronaphthalene into its isomer. The yield of catalyzate during prolonged experiments amounted to 94 - 98% of the 1-chloronaphthalene passed through, the yield of isolated 2-chloronaphthalene being up to 100 g per liter of catalyst within 1 hour of work.

Solidification temperature of the catalyzate obtained within the first hour of work fluctuated within a range of several degrees. The maximum temperature for catalyzate solidification, obtained at 350° reached 23.8°.

Isomerization of 2-Chloronaphthalene.

2-Chloronaphthalene was used as the starting material, obtained by isomerization of 1-chloronaphthalene with subsequent recrystallization from alcohol. To feed in the 2-chloronaphthalene (m.p. 56 - 57°) the standard buret was replaced by a buret with jacket in which water circulated, preheated to 80°. Isomerization of the 2-chloronaphthalene was carried out at 300, 350, 400 and 450° on 80 ml of aluminosilicate catalyst in a stream of hydrogen chloride. Regeneration of catalyst was carried out between experiments by the above-indicated method.

The catalyzate was frozen out at −10°, and the 2-chloronaphthalene which separated was filtered off. The filtrate from 2-chloronaphthalene upon distillation distilled completely in the range 240 - 262°.

Found %: C 73.27, 73.55; H 4.77, 4.82. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.34.

Analysis, and the boiling temperature of the filtrate indicated that it (and hence the catalyzate as well) consisted only of a mixture of the chloronaphthalene isomers. This made it possible to determine the composition of catalyzate from a curve for the solidification temperatures for 1- and 2-chloronaphthalene mixtures. Experimental results are given in Table 8. (see next page)

SUMMARY

1. It has been established that 1-chloronaphthalene isomerizes smoothly into 2-chloronaphthalene upon passage of vapors of the former over aluminosilicate catalyst, or aluminum oxide, along with hydrogen chloride.

2. The isomerization reaction is reversible. Under the same conditions, 2-chloronaphthalene isomerizes into 1-chloronaphthalene. Mixtures of isomers containing about 55% of the 2-chloronaphthalene constitute the equilibrium at 350°.

TABLE 8

Isomerization temperature	2-Chloronaphthalene feed (in g per hour)	Mole ratio of $C_{10}H_7Cl$:HCl	Solidification temperature of the catalyzate within the			Content of 2-chloronaphthalene in catalyzate (in %)
			1st hour	2nd hour	3rd hour	
300*	6.20	1:3	23.4*	–	–	55.0
300	11.50	1:3	27.6	–	–	59.0
350	6.25	1:3	–	23.6**	–	55.0
350	6.50	1:5	20.0	–	–	54.5
400	7.10	1:4	21.6	–	–	53.5
400	11.80	1:3.5	23.0	25.4	26.0*	–
450	6.10	1:5	22.2	–	–	54.0
450	17.85	1:3	23.8	–	–	55.5

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* Within the first two hours.

MECHANISM OF ACTION OF ALUMINUM CHLORIDE CATALYSIS

III. KINETICS OF THE BENZENE ALKYLATION REACTION

N. N. Lebedev

In the preceding articles [1, 2] the structure of complex aluminum halide compounds with alkyl halides, chloroanhydrides and ketones was investigated. The question of role of these complexes has resulted in conflicting opinions for a long time. Some consider them to be essential intermediates, without which reaction is unable to proceed; others consider these complexes to be catalytic poisons which lower the activity of aluminum chloride. The author has used the kinetic method of investigation to clarify the role of these complexes, and other problems as well, which are related to an explanation for the mechanism of action of aluminum chloride catalysis.

Steele [3], using the reaction of benzyl chloride with toluene, studied for the first time the kinetics of alkylation of aromatic hydrocarbons by means of metallic halides. Due to heterogenity of the catalyst, he was unable to obtain satisfactory results. Later, Uhlich and Hayne [4] studied the kinetics of reaction for propyl chloride with benzene in the presence of gallium chloride, the results of which can hardly be extended to include the aluminum chloride reaction, since the authors used another catalyst.

Questions of the effect of structure upon the reactivity of halogen derivatives and aromatic compounds, as well as influence of the medium and other other factors, have remained in these works obscure.

EXPERIMENTAL

The most suitable solvent was found to be nitrobenzene, which dissolves aluminum chloride, readily, and does not deprive it of its catalytic activity. The author purified nitrobenzene by distillation at atmospheric pressure, and sampling of the middle fraction, freezing out, and finally a vacuum distillation, with sampling of the middle fraction only.

A 10 % solution of sublimed aluminum chloride in nitrobenzene was prepared, by varying the dosage of which, the necessary concentration of catalyst in the reaction mixture was obtained.

Benzene was also purified by boiling with aluminum chloride and distilling on a fractionating column, drying finally with metallic sodium.

Cyclohexyl chloride was selected as the alkyl halide due to its low volatility and relative stability with respect to the action of aluminum chloride. Cyclohexyl chloride, prepared by heating one part of cyclohexanol and 4 parts of hydrochloric acid, was thoroughly purified by concentrated sulfuric acid, washed with water, and then sodium carbonate; after drying with calcium chloride and distilling, it had d_4^{20} 0.9760 and n_D^{20} 1.4612.

The method of observation of reaction course was found to be most difficult during study of the kinetics of the alkylation reaction. The only possibility of observation is apparently the evolution of hydrogen chloride. Steele [3] blew it out with a stream of dry hydrogen, having constructed beforehand an empirical curve for blowing out, from which results were calculated. Uhlich and Hayne [4] determined the volume of evolving gas, disregarding solubility of the hydrogen chloride in reaction medium. The latter method seemed to be less accurate, and the author selected the procedure of blowing out hydrogen chloride with a stream of nitrogen, modifying considerably, however, the technique of calculation.

Reaction by the author was carried out in a 60 ml flask with fused-in bubbler for nitrogen and a gas outlet tube. Charging of reactants was carried out through a neck with ground stopper. Nitrogen from the tank was dried with sulfuric acid and solid alkali and its flow rate determined by a rheometer. To avoid carrying solvent away from the reaction mixture, the nitrogen was then passed through a flask containing a mixture of nitrobenzene and benzene, identical in composition with that of the mixture present in the reaction flask. The flask and reaction flask were placed in a thermostat, where the required temperature was maintained within an accuracy of ± 0.05°. Nitrogen, together with hydrogen chloride, was passed into an absorber of distilled water, where the hydrogen

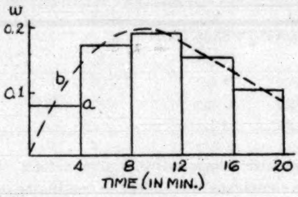


Fig. 1. Relationship of HCl Blow-Out Rate with Time. Explanation in Text

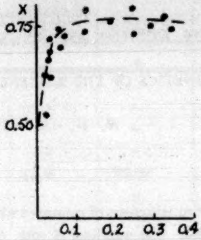


Fig. 2. Relationship between Saturation Coefficient (x) and Rate of Blow-Out (W)

chloride was absorbed. By means of a three-way stopcock it was possible, after a measured time interval determined by a second watch, to pass the gases into another absorber. Titration of the solutions from the absorbing vessels with 0.1 N-NaOH gave the amount of hydrogen chloride evolved during a defined time interval for the reaction.

If n_z = total amount of hydrogen chloride absorbed in the absorber, then the amount of hydrogen chloride formed will be greater in amount than was contained in the gas space of the flask and dissolved in the reaction mixture:

$$\Sigma n = n_z + n_{gas} + n_{dissolved}$$

For the most accurate determination of hydrogen chloride concentration in the gaseous phase, a diagram was constructed (a) according to the experimental data with the coordinates: time of blow-out of hydrogen chloride (W) versus Time (Fig. 1). On the basis of this diagram a curve was then plotted for the true rates of blow-out (b). Using as symbols V = total volume of gases/minute, K = coefficient of solubility for hydrogen chloride, $\underline{x}$ = degree of saturation during bubbling, and taking into account that the volume of gas phase amounted to 40 ml, and the reaction volume 20 ml, we then have

$$\Sigma n = n_z + \frac{W \cdot 40}{V} + \frac{W \cdot K \cdot 20}{V \cdot x} = n_z + \frac{W}{V}\left(40 + \frac{20K}{x}\right).$$

The total volume of gases in its turn is composed of rates for nitrogen, hydrogen chloride, and carrying away of benzene vapors.

Hydrogen chloride solubility coefficients in benzene and nitrobenzene as determined specially by the authors, are given in Table 1 (concentration in the gas and in the liquid phases given in moles/liter.

TABLE 1
Solubility Coefficients of Hydrogen Chloride

Solvent	Temperature			
	20°	30°	40°	50°
Nitrobenzene	16.4	13.7	11.4	9.5
Benzene	11.5	9.3	7.5	6.0

The solubility of hydrogen chloride in benzene-nitrobenzene mixture was calculated according to the principle of additivity.

The saturation coefficient, $\underline{x}$, was determined by special experiments in which hydrogen chloride was blown through a solution of benzene and nitrobenzene. The value was found to depend upon the hydrogen chloride concentration, as indicated in Fig. 2, where blowing rates in millimoles/min. were plotted on the abscissa axis and the saturation coefficient, $\underline{x}$, on the ordinate axis.

Due to the low moisture in starting products while blowing out the reaction mixture, which did not contain cyclohexyl chloride, some hydrogen chloride was evolved; in the experimental results, therefore, a correction was introduced by subtracting from the titration data the values resulting from the blank experiment carried out under the same conditions, but without cyclohexyl chloride.

Confirmatory experiments carried out by the authors with various volumes of reaction mass and nitrogen flow rates, gave deviations from the rate constants averaging in the range of ±2%, which indicated sufficient accuracy for the procedure and technique of calculation as developed by the author.

The rate constants (concentrations in m/l, time in min.) which are quoted farther on, are average values for not less than 3 experiments, calculating by the graphic procedure.

Before starting experiments, the author made certain that cyclohexyl chloride in nitrobenzene solution is sufficiently stable with respect to the action of aluminum chloride up to 50°, and that hydrogen chloride is not split out under these conditions. Thus, only an alkylation reaction is possible:

$$C_6H_{11}Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_5C_6H_{11} + HCl.$$

As has been indicated by Kursanov [5], Mayes and Turner [6], cyclohexylbenzene results in good yield, in this reaction, which makes it quite suitable for study of the kinetics. In order to avoid dealkylation, not less than 7-fold excess of benzene was used everywhere.

The Effect of Alkyl Halide Concentration. In this series of experiments, only the initial concentration of cyclohexyl chloride was varied, all other factors remaining constant (temperature 40°, $AlCl_3$ concentration 0.1 M/ /liter). The results obtained are given in Table 2.

TABLE 2

Composition of the reaction medium (in volume %)		Initial concentration of cyclohexyl chloride (in M/l).	Rate constant, K_1	Time for half-decomposition (in min.)
Benzene	Nitrobenzene			
75.0	23.7	0.100	0.0190	36.5
75.0	22.5	0.200	0.0194	35.7
75.0	21.5	0.300	0.0195	35.5
12.5	86.2	0.100	0.128	5.4
12.5	85.0	0.200	0.132	5.25
12.5	84.0	0.300	0.131	5.3

With variation in initial concentration of cyclohexyl chloride, the time interval remained almost constant in which the half-reacted (cyclohexyl chloride), and the results of each individual experiment are superimposed well upon a straight line for log C versus time. All of these facts indicated that there was monomolecularity of the alkylation reaction in relation to concentration of alkyl halide:

$$v = k_1[RCl].$$

These data also make it possible to conclude that hydrogen chloride has no effect of any kind upon the reaction rate.

Effect of Benzene Concentration. The difficulty in studying effects of benzene concentration stems from the large effect of medium upon reaction rate, as can be seen from the preceding table. At the same time, the necessity for maintaining excess benzene in the alkylation reaction makes the components of the solvent of importance. In order to maintain the same approximate concentration of medium, and yet modify the benzene concentration, a portion of the latter was replaced by decalin . In the first three experiments of Table 3, this replacement was carried out in such a manner that the volumetric concentration of nitrobenzene remained constant, and in the last three experiments, its molar concentration remained constant.

TABLE 3

The Concentration of $AlCl_3$ was 0.100 m/liter, and of Cyclohexyl Chloride 0.2 m/liter, Temperature 40°.

Experiment No.	Composition of medium (in volume %)			Concentration of benzene (in m/liter)	Rate constant	
	Benzene	Decalin	Nitrobenzene		k_1	k_2
1	25.0	–	72.5	2.81	0.147	0.052
2	12.5	12.5	72.5	1.41	0.0789	0.056
3	6.25	18.75	72.5	0.70	0.0440	0.063
4	25.0	–	72.5	2.81	0.145	0.052
5	12.5	18.0	67.0	1.41	0.0660	0.047
6	6.25	27.0	64.25	0.70	0.0306	0.044

Increase in the k_2 constants is explainable in the first instance by an increase in the molar quantity of nitrobenzene upon replacing benzene with decalin and their decrease in the second series by the high inertness of decalin as a solvent, compared to benzene.

Despite certain deviations, the data obtained make it possible to consider alkylation reactions as monomolecular with respect to benzene:

$$v = k_2[RCl][C_6H_6].$$

Effect of the Medium. Effect of the medium on alkylation reactions as noted above was particularly studied by the author through modification of the ratio of benzene to nitrobenzene in the reaction mixture, other conditions being constant (see Table 4).

Table 4 data are presented in Fig. 3a, indicating large increase in rate of reaction with increase in nitrobenzene content in the reaction mixture. Extrapolation of the curve to benzene and nitrobenzene concentrations of 100 % give, respectively, k_2 constants of 0.0014, and 0.2, i.e., a rate increase of more than 100-fold with change in solvent.

TABLE 4

Temperature 40°, concentration of $AlCl_3$ 0.100 m/liter, cyclohexyl chloride 0.2 m/liter.

Composition of medium (in volume %)		Rate constant	
Benzene	Nitrobenzene	k_1	k_2
5.0	92.5	0.0807	0.143
12.5	85.0	0.132	0.094
25.0	72.5	0.146	0.052
50.0	47.5	0.0690	0.012
75.0	22.5	0.0194	0.0023
87.5	10.0	0.0180	0.0018

Activation Energy. To determine the energy of activation, experiments were carried out at temperatures of 20, 30, 40, and 50 ± 0.05°, results of which are given in Table 5. The initial concentration of cyclohexyl chloride was 0.200 m. The activation energy was calculated by the graphical method.

Thus, with variation in composition of the medium, somewhat different values for the activation energy were obtained; however, the deviations observed lay on the boundary of possible experimental error.

Effect of Aluminum Chloride Concentration. Maintaining all other conditions constant, the author carried out experiments in which the concentration of aluminum chloride was varied. Experimental results for various compositions of the medium are given in Table 6, where in the last column are placed values for the formal order of the reaction with respect to aluminum chloride, n, calculated according to each pair of rate constants from the equation

$$n = \frac{\log k_1 - \log k_1'}{\log c_{AlCl_3} - \log c'_{AlCl_3}}.$$

If the change in reaction order relative to composition of the medium is presented graphically, and if the curve is extrapolated to a benzene concentration of 100 %, then the picture presented in Fig. 3b, will result.

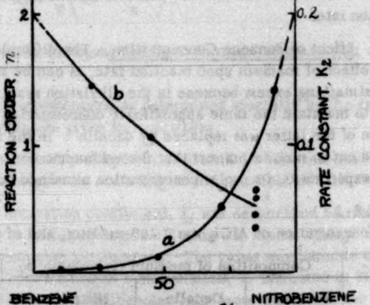


Fig. 3. Effect of medium on rate and order of reaction.

EVALUATION OF RESULTS

It follows from the data that the alkylation reaction for benzene with alkyl halide in the presence of aluminum chloride proceeds according to the following kinetic equation:

$$v = k[AlCl_3]^n[RCl][C_6H_6].$$

The order of reaction n with respect to aluminum chloride is dependent upon the composition of the medium; in nitrobenzene it approximates 0.5; extrapolation value for pure benzene is near 2, and in a mixture of the two solvents, an intermediate value results (see Fig. 3, b). Change in order of reaction indicates two different mechanisms, occurring with variation in properties of the medium.

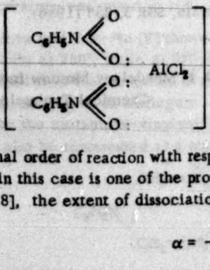
In clarifying the results obtained, it should be borne in mind that aluminum chloride forms a complex with nitrobenzene, with a polar structure [2]. The high thermal dissolution effect of aluminum chloride in nitrobenzene (12200 cal/mole) [7] excludes the possibility of free aluminum chloride being present which is not bound up with the complex. Its solutions in nitrobenzene possess an electroconductivity [8] due to dissociation of the complex into ions [2]:

TABLE 5

Composition of medium (in volume %) benzene	nitrobenzene	$AlCl_3$ concentration (m/liter)	Temperature	Rate constant K_1	Activation energy (cal/mole)
12.5	85.0	0.203	20.0°	0.0205	18700
		0.203	30.0	0.0635	
		0.100	30.0	0.0476	
		0.100	40.0	0.130	
		0.025	40.0	0.0520	
		0.025	50.0	0.122	
75.0	22.5	0.203	30.0	0.0217	17500
		0.203	40.0	0.0550	
		0.100	40.0	0.0193	
		0.100	50.0	0.0450	

TABLE 6

Composition of medium (in volume %) benzene	nitrobenzene	Temperature	Concentration of $AlCl_3$ (m/liter)	Rate constant K_1	Order of reaction, n
12.5	85.0	30.0°	0.025	0.0200	0.64
12.5	85.0	30.0	0.049	0.0308	0.59
12.5	85.0	30.0	0.100	0.0470	0.44
12.5	85.0	30.0	0.203	0.0642	0.35
12.5	85.0	30.0	0.410	0.0820	
50.0	47.5	40.0	0.049	0.0327	1.05
50.0	47.5	40.0	0.100	0.0690	1.05
50.0	47.5	40.0	0.203	0.146	
75.0	22.5	40.0	0.100	0.0196	1.44
75.0	22.5	40.0	0.203	0.0550	
75.0	22.5	50.0	0.100	0.450	1.46
75.0	22.5	50.0	0.203	0.125	



$$[AlCl_4] \rightleftharpoons [(C_6H_5NO_2)_2AlCl_2]^+ + [AlCl_4]^-.$$

A fractional order of reaction with respect to aluminum chloride in nitrobenzene medium indicates that the actual catalyst in this case is one of the products of complex dissociation. Inasmuch as the constant for this dissociationa is small [8], the extent of dissociation therefore is

$$\alpha = \frac{-K + \sqrt{K^2 + 4Kc}}{2c} \approx \sqrt{\frac{K}{c_{AlCl_3}}}$$

and the rate equation takes the form of

$$v = k'\alpha c_{AlCl_3}[RCl][C_6H_6] = kc^{0.5}_{AlCl_3}[RCl][C_6H_6],$$

which is indeed observed in the reaction course carried out in nitrobenzene.

Ionic character of the catalysis is confirmed by the strong influence of medium upon the rate of this reaction, and in the well-ionizing solvent (nitrobenzene) it proceeds more rapidly than in benzene.

Of the two dissociation products being formed, the true catalyst for the process can only be the cation, inasmuch as the anion $(AlCl_4)^-$ is found in all complexes of aluminum chloride, also catalytically inactive (for example its complexes with ketones).

Upon changing the medium and moving to poorly-ionizing solvents, the cation concentration is strongly decreased due to weak dissociation of the complex. Instead of a rapid catalysis proceeding with the cation, there is a slow reaction in which the role of active reagent is played by the undissociated molecules of catalyst.

The general kinetic equation in such a case will be as follows:

$$\nu = k_i([AlCl_3]^{0.5} + k_s\ [AlCl_3]^2)\ [RCl]\ [C_6H_6].$$

where k_i = constant for the rapid reaction rate of ionic catalysis, k_s = rate constant for slow reaction of a bimolecular catalysis.

Superimposition of both mechanisms in various ratios with respect to properties of the medium results in an intermediate value for the order of reaction for aluminum chloride.

SUMMARY

1. A procedure has been developed and the kinetics studied for the reaction of cyclohexyl chloride with benzene in the presence of aluminum chloride and in mixtures of benzene and nitrobenzene.

2. The reaction has been found to be monomolecular with respect to alkyl halide and benzene, but has an intermediate value from 0.5 to 2nd order for aluminum chloride, depending upon the composition of the medium.

3. Activation energies for the reaction have been determined.

4. A strong effect of medium upon the reaction rate has been observed.

5. The results obtained are interpreted by the existence of two mechanisms for the process — a rapid reaction of ionic catalysis in highly ionizing solvent, and a slow reaction of bimolecular catalysis in weakly ionizing medium.

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* See Consultants Bureau Translation, page 1975.

BEHAVIOR OF N-(β-HYDROXYETHYL)-ANILINE AND N-(β-HYDROXYETHYL)-o-TOLUIDINE IN THE PRESENCE OF ALUMINOSILICATE

Yu. K. Yuryev and L. F. Gorin

The synthesis of compounds of the indole and dihydroindole series from the readily available N-(β-hydroxyethyl)-arylamines is of great interest.

According to the data of Knorr [1], only an insignificant quantity of indole could be isolated in experiments involving the closure of the ring in N-(β-hydroxyethyl)-aniline with the aid of various condensing agents. Alkaline fusion [2] at 240-280° in a reducing atmosphere led to the splitting off of two hydrogen molecules and to the formation of indoxyl in a yield of 60%. Upon heating with phosphorus pentoxide in xylene [3], N,N'-diphenylpiperazine was obtained together with an insignificant quantity of a fraction with a b.p. of 220-270° which, in the opinion of the authors, contained dihydroindole.

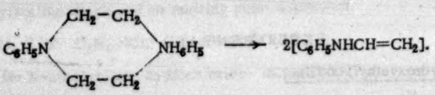
Shorygin and Belov [4] described a series of experiments involving the dehydration of N-(β-hydroxyethyl)-aniline. When conducted over Glukhov clay at 450-520°, N-(β-hydroxyethyl)-aniline yielded a viscous yellow catalyzate from which only a small quantity of aniline could be distilled off; upon heating with anhydrous oxalic acid, it did not change; it resinified under the action of aluminum chloride; it yielded the dimer of N-vinylaniline upon heating 2-3 hours with sodium to 260-280°.

Yuryev and Novitsky [5] obtained N,N'-diphenylpiperazine by heating N-(β-hydroxyethyl)-aniline with an aluminosilicate cracking catalyst at 240°.

In the present work the possibility of obtaining indole and dihydroindole from N-(β-hydroxyethyl)-aniline in the presence of the same catalyst, but at a much higher temperature, was studied. It was established that at 300° the dehydration of N-(β-hydroxyethyl)-aniline does not proceed simply, but is complicated by dehydrogenation, hydrogenation and alkylation of the reaction products. The following were isolated from the mixture of reaction products: aniline (chief reaction product), 4-ethylaniline, indole, skatole and diphenylpiperazine. It was shown by the preparation of crystalline derivatives that p-toluidine, N-ethylaniline, dihydroindole, 2,4-diethylaniline and quinaldine were also contained in the reaction products. Finally, we isolated a mixture of alkylindoles with a b.p. of 112-124° (4 mm), in which the presence of diethyl- and triethylindoles, the structures of which were not established, was proved by preparing the picrates. It should be noted that no appreciable evolution of gas or formation of low-boiling reaction products was observed.

The results obtained in the present work make it possible to express the following considerations concerning the mechanism of the reaction studied by us. As was indicated above, the dehydration of N-(β-hydroxyethyl)-aniline, in the presence of aluminosilicate at 240° [5], leads to the formation of N,N'-diphenylpiperazine, while when the temperature was raised to 300°, it was possible to isolate only an insignificant quantity of the latter (2%).

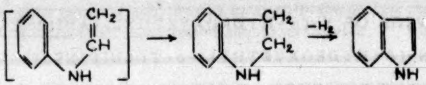
Topchieva and Yun-Pin [6] showed for the first time that ethyl alcohol yields diethyl ether in the presence of aluminosilicate at 250°, while at 300-320°, the chief reaction product is ethylene. At 300-320°, diethyl ether is also dehydrated with the formation of ethylene. We assume that the dehydration of N-(β-hydroxyethyl)-aniline also proceeds according to an analogous scheme; the product of its dehydration over aluminosilicate at 300° should consequently be the unstable N-vinylaniline: $C_6H_5NHCH_2CH_2OH \rightarrow [C_6H_5NHCH{=}CH_2] + H_2O$. The formation of the latter can also be represented as a result of the cleavage of N,N'-diphenylpiperazine:



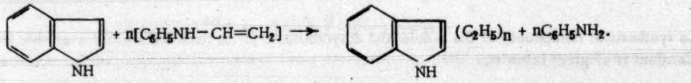
$$C_6H_5N\langle^{CH_2-CH_2}_{CH_2-CH_2}\rangle NH_6H_5 \longrightarrow 2[C_6H_5NHCH{=}CH_2].$$

N-Vinylaniline undergoes the following further series of reactions:

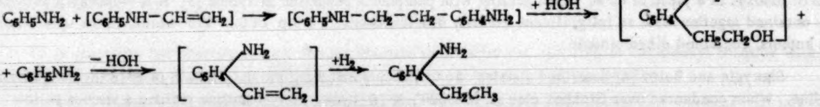
1. Intramolecular alkylation with the formation of dihydroindole which loses hydrogen to yield indole:



A mixture of alkylindoles and aniline was obtained as a result of the further alkylation of indole with vinylaniline with subsequent hydrolysis, cleavage of water from the ethanolindoles formed and addition of hydrogen to vinylindole:



2. Alkylation of aniline with subsequent hydrolysis of the alkylation product, cleavage of water from the formed 4-(β-hydroxyethyl)-aniline, and addition of hydrogen to 4-vinylaniline led to the formation of 4-ethylaniline:



$$C_6H_5NH_2 + [C_6H_5NH-CH=CH_2] \longrightarrow [C_6H_5NH-CH_2-CH_2-C_6H_4NH_2] \xrightarrow{+\,HOH} \left[C_6H_4 \begin{matrix} NH_2 \\ CH_2CH_2OH \end{matrix} \right] +$$

$$+\, C_6H_5NH_2 \xrightarrow{-\,HOH} \left[C_6H_4 \begin{matrix} NH_2 \\ CH=CH_2 \end{matrix} \right] \xrightarrow{+H_2} C_6H_4 \begin{matrix} NH_2 \\ CH_2CH_3 \end{matrix}$$

2,4-diethylaniline was obtained by the further alkylation of 4-ethylaniline.

3. Addition of hydrogen with the formation of N-ethylaniline:

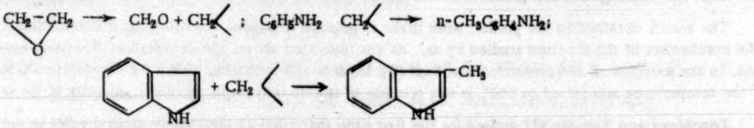
$$[C_6H_5NH-CH=CH_2] \xrightarrow{+H_2} C_6H_5NHC_2H_5.$$

4. Isomerization into acetanil and formation of N-ethylaniline from it as a result of the addition of hydrogen:

$$[C_6H_5NH-CH=CH_2] \longrightarrow [C_6H_5N=CH-CH_3] \xrightarrow{+\,H_2} C_6H_5NHC_2H_5.$$

Along with these processes, there no doubt occurs the decomposition of N-(β-hydroxyethyl)-aniline into aniline and ethylene oxide which isomerizes into acetaldehyde; the latter condenses with aniline to form quinaldine.

The mechanism of formation of p-toluidine and skatole is not clear. If, however, it is assumed that the decomposition of ethylene oxide into formaldehyde and the methyl radical [7] is possible only to an insignificant extent, then the formation of insignificant quantities of p-toluidine and skatole can be represented as the result of the alkylation of aniline and, respectively, indole with the methyl radical [8].



N-(β-Hydroxyethyl)-o-toluidine behaves similarly under analogous conditions. o-Toluidine (the chief reaction product), 2-methyl-4-ethylaniline and 7-methylindole were isolated from the complex mixture of reaction products.

We consider the formation of 7-methylindole in the absence of tetrahydroquinoline or quinoline in the reaction products as a confirmation of the mechanism which we proposed for the dehydration of N-(β-hydroxyethyl)-aniline.

EXPERIMENTAL

Dehydration of N-(β-Hydroxyethyl)-aniline.

N-(β-Hydroxyethyl)-aniline (b.p. 176° at 19 mm; n_D^{20} 1.5763; d_4^{20} 1.0945) [9] was conducted in a stream of nitrogen over aluminosilicate cracking catalyst at 300° at a volumetric rate of 0.5 ml/ml of catalyst per hour. About 30 g of material was introduced in each experiment, after which the catalyst was regenerated [10]. 253 g of catalyzate (of which 40 g was water) was obtained from 300 g of N-(β-hydroxyethyl)-aniline.

The following fractions were isolated by two-fold fractionation of the oily portion of the catalyzate (dried with calcined potash) in a vacuum at 5 mm from a flask with a fractionating column: 1st b.p. 60-61.5°, 135.5 g; 2nd, b.p. 61.5-85°, 6.9 g; 3rd, b.p. 85-118°, 18.4 g; 4th b.p. 118-155°, 33.4 g; 5th, b.p. 155-186°, 4.0 g; residue 11.5 g.

Crystals precipitated from the 5th fraction and from the residue, and their quantity was increased by freezing out. After having been filtered off, washed with ether and recrystallized from alcohol, they melted at 163° and consisted of N,N'-diphenylpiperazine (5.5 g); a mixed sample with known diphenylpiperazine displayed no melting point depression.

The picrate (from alcohol) consisted of yellow needles with an m.p. of 172-173°; a mixed sample with the known picrate of N,N'-diphenylpiperazine displayed no melting point depression.

The literature data for N,N'-diphenylpiperazine are: m.p. 163° [5]; m.p. 163-164° [11]; m.p. 163.5-164.5° [12]; picrate: m.p. 172-173° [5].

Fractions Nos. 1,2,3 and 4 were fractionated twice more in a vacuum at 10 mm in a column with an efficiency of 18 theoretical plates. The results obtained in the second fractionation with the column, are presented in Table 1.

TABLE 1

Fraction No.	B.p. at 10 mm	Quantity (in g)	n_D^{20}	d_4^{20}	Fraction No.	B.p. at 10 mm	Quantity (in g)	n_D^{20}	d_4^{20}
1	69.0 - 69.5°	133.5	1.5853	1.0221	11	100.0 - 111.5°	0.58	1.5683	—
2	69.5 - 76.0	1.7	1.5846	—	12	111.5 - 117.5	0.7	1.5801	—
3	76.0 - 80.0	0.9	1.5778	—	13	117.5 - 119.5	1.9	1.6014	1.0590
4	80.0 - 81.5	1.1	1.5645	0.9831	14	119.5 - 127.5	2.2	1.6032	—
5	81.5 - 85.5	0.9	1.5618	—	15	127.5 - 130.0	2.1	1.6078	—
6	85.5 - 90.0	0.2	1.5610	—	16	130.0 - 136.5	3.6	1.5943	—
7	90.0 - 92.5	0.9	1.5565	—	17	136.5 - 146.0	3.7	1.5913	—
8	92.5 - 93.0	1.7	1.5558	0.9680	18	146.0 - 148.5	6.9	1.5870	—
9	93.0 - 96.0	0.9	1.5575	—	19	148.5 - 152.0	2.6	1.5895	—
10	96.0 - 100.0	0.6	1.5603	—	Residue	. . . .	15.9	—	—

a) Aniline. Fractions Nos. 1 and 2 consisted of aniline. The yield was 135.2 g (65.5%). The acetanilide obtained from them melted at 115°, and a mixed sample with known acetanilide displayed no melting point depression.

b) p-Toluidine. The bulk of Fraction No. 4 consisted of p-toluidine. The N-acetyl-p-toluidine (0.6 g) obtained from it melted at 145.0-146.0° after recrystallization from alcohol; a mixed sample with known N-acetyl-p-toluidine displayed no melting point depression. The picrate (from benzene) melted at 180°; a mixed sample with the known picrate of p-toluidine displayed no melting point depression.

The literature data for p-toluidine are: b.p. 82.2° (10 mm), m.p. 45° [13]; N-acetyl-p-toluidine; m.p. 145.5 [14]; p-toluidine picrate: m.p. 180° (with decomposition) [15].

c) N-ethylaniline: 0.8 g of Fraction No. 5 was stirred with 0.6 ml of concentrated hydrochloric acid [16]. The hydrochloride crystals which were formed were filtered off and washed with concentrated hydrochloric acid. After recrystallization from alcohol the hydrochloride melted at 176°, and a mixed sample with the known hydrochloride of N-ethylaniline displayed no melting point depression.

Found %: N 8.71, 8.89. $C_8H_{12}NCl$. Calculated %: N 8.89.

Literature data for N-ethylaniline hydrochloride: m.p. 176° [17].

d) 4-Ethylaniline: Fraction No. 8 with a b.p. of 92.5 - 93° (10 mm), n_D^{20} 1.5558; d_4^{20} 0.9680; MR 40.21;

calculated 38.96, consisted of 4-ethylaniline.

Found %: C 79.27, 79.52; H 9.05, 8.98; N 11.19, 11.26. $C_8H_{11}N$. Calculated %: C 79.30; H 9.15; N 11.56.

After recrystallization from water, the 4-ethylacetanilide (0.4 g) [18] melted at 94°.

Found %: N 8.78. $C_{10}H_{13}ON$. Calculated %: N 9.15.

4-Ethylaniline picrate (from benzene) melted at 168°.

Found %: N 16.24, 16.10. $C_{14}H_{14}O_7N_4$. Calculated %: N 15.99.

The 4-ethylaniline sulfate (0.8 g) obtained by mixing 2 N sulfuric acid with a solution of 0.5 g of Fraction No. 8 in 0.8 ml of alcohol, and dilution with water until the solution became turbid [19], melted at 239° after recrystallization from hot water.

Found %: H_2SO_4 27.13, 27.12 (by titration with phenolphthalein as indicator). $C_{16}H_{22}N_2 \cdot H_2SO_4$. Calculated %: H_2SO_4 27.14.

Literature data for 4-ethylaniline: b.p. 213-214°; n_D^{22} 1.5529; d_4^{22} 0.975 [20]; b.p. 93.8° (10 mm) [13]; 4-ethylacetanilide: m.p. 95° [21]; 4-ethylaniline sulfate: m.p. 239° [19].

Fractions Nos. 11-19 gave a positive reaction for indole (pine shavings, moistened with hydrochloric acid, became red colored).

To isolate indole and determine the composition of Fractions Nos. 10-15, on the basis of their solubility in ether, these fractions were subjected to fractional precipitation in ethereal solution by picric acid. After the slightly ether-soluble yellow picrates had been precipitated, the ethereal solution was red-colored due to the readily soluble indole picrate [22]. The picrates with an identical melting point, obtained from a given fraction, were combined. The identity of picrates with identical melting points but obtained from different fractions, was established by a mixed melting point test.

The results of the fractional precipitation of the picrates are presented in Table 2.

e) Dihydroindole: The picrates of Nos. 4, 5, 8, and 11 consisted of dihydroindole picrate. A mixed sample of these picrates displayed no melting point depression: m.p. 173-174° (0.3 g).

Found %: N 16.13, 16.06. $C_{14}H_{12}O_7N_4$. Calculated %: N 16.16.

On adding an alcoholic solution of oxalic acid to 0.2 g of Fraction No. 12, white, thread-like crystals of dihydroindole oxalate were obtained which melted at 127-128° after recrystallization from aqueous alcohol. Upon being heated in 96% alcohol, they were converted into the neutral oxalate, which crystallized with three molecules of water.

5.180 mg substance: 0.330 ml N_2 (23°, 748 mm). Found %: N 7.23. $C_{18}H_{16}O_2N_2 \cdot 3H_2O$. Calculated %: N 7.34.

Literature data for dihydroindole: b.p. 228-231°; n_D^{25} 1.5891 [23]; b.p. 100-101° (12 mm) [22]; dihydroindole picrate: m.p. 174° [23]; acid oxalate of dihydroindole: m.p. 127-128° [24].

f) 2,4-Diethylaniline: A mixed sample of the picrates of Nos. 6, 9, and 13 displayed no melting point depression. In all, 2.1 g of a picrate with a m.p. of 184° was obtained. The picrate was decomposed with ammonia and the base extracted with ether. The ethereal extract was washed with water and dried by fusing with sodium hydroxide. After distilling off the ether and fractionally distilling the residue, 0.5 g of an oil was obtained which consisted of 2,4-diethylaniline. 2,4-Diethylacetanilide was obtained by heating 0.2 g of the oil with 0.2 g of glacial acetic acid [25]; after recrystallization from alcohol and vacuum sublimation, it melted at 103-104°.

The benzenesulfonamide of 2,4-diethylaniline was obtained as follows: 0.3 g of the oil was shaken with 0.6 g of benzenesulfochloride. After recrystallization from alcohol, the sulfonamide (soluble in alkali) melted at 112° and consisted of the benzenesulfonamide of 2,4-diethylaniline.

Found %: N 3.75, 3.57. $C_{16}H_{19}O_2NS$. Calculated %: N 3.94.

Literature data for 2,4-diethylaniline: b.p. 140-142° (20 mm); 2,4-diethylacetanilide: m.p. 104° [25].

g) Quinaldine: The picrates of Nos. 16 and 18, with a m.p. of 192°, consisted of quinaldine picrate. A mixed sample with known quinaldine picrate displayed no melting point depression: m.p. 192°.

TABLE 2

Fraction		Picrates obtained				
No.	Quantity (in g)	Picrate No.	M.p. of picrate	Quantity (in g)	M.p. after recrystallization	Designation of the picrate
10	0.6	1	168°	0.9	168°	4-Ethylaniline picrate (a mixed sample with the picrate from Fraction No. 8 displayed no melting point depression)
		2	161	0.4	–	
11	0.5	3	158	0.4	–	–
		4	167	0.4	173	Dihydroindole picrate
		5	172	0.1	173 - 174	Dihydroindole picrate
12	0.5	6	183	0.3	184	2,4-Diethylaniline picrate
		7	165	0.3	–	–
		8	170	0.2	174	Dihydroindole picrate
13	1.9	9	182	1.6	184	2,4-Diethylaniline picrate
		10	162	0.5	–	–
		11	168	0.2	173 - 174	Dihydroindole picrate
		12	176	0.1	–	–
14	2.2	13	183	0.2	184	2,4-Diethylaniline picrate
		14	171	0.3	–	–
		15	184	0.3	–	–
		16	188	0.4	192	Quinaldine picrate
15	2.1	17	179	0.2	–	–
		18	187	0.3	192	Quinaldine picrate

Found %: N 13.68, 14.59. $C_{16}H_{12}O_7N_4$. Calculated %: N 15.04.

Literature data for quinaldine picrate: m.p. 191-192° [26].

h) Indole: The ethereal solutions, left after precipitating the difficultly ether-soluble picrates from Fractions Nos. 11 - 15, were combined, treated with ammonia solution, diluted with hydrochloric acid and then with soda solution. After drying with calcined potash and distilling off the ether in a vacuum, the residue crystallized. 2.7 g of a substance with an m.p. of 43° was obtained. After recrystallization from n-hexane and vacuum sublimation, the substance melted at 52° and consisted of indole. A mixed sample with known indole displayed no melting point depression. The indole picrate (from benzene) consisted of shiny red needles with an m.p. of 181-182° (upon rapid fusion in bulk); a mixed sample with known indole picrate displayed no melting point depression.

Found %: N 16.15, 16.06. $C_{14}H_{10}O_7N_4$. Calculated %: N 16.19.

Literature data for indole: b.p. 123° (5 mm), m.p. 52° [27]; indole picrate: m.p. 181-182° [28].

i) Skatole: 0.3 g of crystals with an m.p. of 82° were isolated by freezing out from a solution of 3.4 g of Fraction No. 16 (b.p. 130 - 136.5° at 10 mm). After recrystallization from water and vacuum sublimation, the crystals melted at 92 - 93° and consisted of skatole. A mixed sample with known skatole displayed no melting point depression (m.p. 93°).

Found %: N 10.95, 11.15. C_9H_9N. Calculated %: N 10.68.

Skatole picrate (from benzene) melted at 170 - 171° (upon rapid fusion in bulk); a mixed sample with known skatole picrate displayed no melting point depression.

Found %: N 15.49. $C_{15}H_{12}O_7N_4$. Calculated %: N 15.54.

Literature data for skatole: m.p. 95°; skatole picrate: m.p. 170 - 171° [29].

j) Alkylindoles: Fractions Nos. 17, 18, 19 and the residue from the fractional distillation were steam distilled. The initial N-(β-hydroxyethyl)-aniline was not detected in the non-steam-distillable residue. The distillate was extracted with ether; the ethereal extract was repeatedly washed with dilute hydrochloric acid and water and dried with potash. After distilling off the ether, the residue was vacuum distilled; 15 g of an oil with an indole odor and a b.p. of 112 - 124° (8 mm) was isolated (it gave an indole reaction on pine shavings, moistened with hydrochloric acid) which resinified as a result of the action of concentrated hydrochloric acid and gave a red liquid with nitric acid.

Skatole picrate (0.3 g) with an m.p. of 171° was obtained by fractional precipitation of the picrates from the benzene solution.

After concentration of the filtrate and addition of petroleum ether [30], an orange-red picrate with an m.p. of 143° precipitated from it. The picrate obtained decomposed upon solution in all of the solvents used. Decomposition of the picrate with ammonia, distillation of the base and secondary precipitation gave a picrate with the same melting point.

5.587 mg substance: 0.631 ml N_2 (26°, 747 mm). 5.839 mg substance: 0.650 ml N_2 (23°, 754 mm). Found %: N 12.87, 12.74. $C_{20}H_{22}O_7N_4$. Calculated %: N 13.02.

The analytical data agree with those of triethylindole picrate.

A picrate with an m.p. of 136° was obtained from the filtrate after precipitating the picrate with an m.p. of 143° and after concentration and addition of petroleum ether. Subsequent concentration of the filtrate and repeated precipitation with petroleum ether led to a picrate with an m.p. of 124° (red-brown needles). A second reprecipitation of the picrate did not change its melting point.

5.335 mg substance: 0.649 ml N_2 (26°, 751 mm). 5.013 mg substance: 0.605 ml N_2 (23°, 751 mm). Found %: N 13.72, 13.75. $C_{18}H_{18}O_7N_4$. Calculated %: N 13.93.

The analytical data agree with those for diethylindole picrate.

5 g of a mixture of the ethylindoles was heated for 5 hours with excess acetic anhydride. After distilling off the acetic anhydride and acetic acid, the residue was steam distilled. About 1 g of base distilled off, which was extracted with ether, dried with potash and after distilling off the ether, was vacuum distilled. The picrate, obtained from the benzene solution by precipitation with petroleum ether, melted at 143°. A mixed sample with the previously prepared triethylindole picrate displayed no melting point depression. It can consequently be concluded that one of the radicals in the triethylindole is bound to the nitrogen atom.

Dehydration of N-(β-Hydroxyethyl)-o-toluidine

N-(β-Hydroxyethyl)-o-toluidine [9] (b.p. 146° at 3 mm; n_D^{20} 1.5690; d_4^{20} 1.0794) was conducted over aluminosilicate cracking catalyst under conditions analogous to those described above, i.e., at 300° at a volumetric rate of 0.5 ml/ml of catalyst per hour. 300 g in all of N-(β-hydroxyethyl)-o-toluidine was conducted over the catalyst. No appreciable gas formation was observed. 220 g of catalyzate which contained 27 g of water, was obtained. After separating the water, the catalyzate, dried with calcined potash, was distilled initially from a flask with a fractionating column; no low-boiling substances were detected in the reaction product. By subsequent redistillation at 7 mm, the following fractions were isolated: 1st b.p. 71.5 - 72.5°, 113 g; 2nd b.p. 72.5 - 87°, 14 g; 3rd b.p. 87 - 108°, 4 g; 4th b.p. 108 - 128°, 20 g; 5th b.p. 128 - 140°, 14.6 g; residue 22 g.

Further fractionation with a column with an efficiency of 18 theoretical plates in a vacuum at 7 mm gave the results presented in Table 3.

a) o-Toluidine: Fraction No. 1 (b.p. 71.5 - 72° at 7 mm; n_D^{20} 1.5723; d_4^{20} 0.9978) consisted of o-toluidine. The yield was 112.5 g (54.0 %). The N-acetyl-o-toluidine obtained from it melted at 110°, and a mixed sample with known N-acetyl-o-toluidine displayed no melting point depression.

Literature data for o-toluidine: b.p. 82° (10 mm) [13], b.p. 199.7° (760 mm) [13]; n_D^{20} 1.57276; d_4^{20} 0.9986 [31]; N-acetyl-o-toluidide: m.p. 110° [32].

b) 2-Methyl-4-ethylaniline: Fraction No. 4 (2.3 g; b.p. 106.5 - 107° at 7 mm; n_D^{20} 1.5514; d_4^{20} 0.9644; MR_D 44.74. $C_9H_{13}N\digamma_3$. Calculated: 43.58) consisted of 2-methyl-4-ethylaniline.

Found %: C 80.09, 79.94; H 9.66, 9.53; N 10.39, 10.58. $C_9H_{13}N$. Calculated %: C 80.03; H 9.7; N 10.36.

After recrystallization from dilute alcohol, the acetyl derivative of 2-methyl-4-ethylaniline [21] melted at 105 - 105.5°.

Found %: N 7.86, 7.91. $C_{11}H_{15}ON$. Calculated %: N 7.90.

TABLE 3

Fraction No.	Boiling point	n_D^{20}	d_4^{20}	Quantity (in g)	Fraction No.	Boiling point	n_D^{20}	d_4^{20}	Quantity (in g)
1	71.5 - 72.0°	1.5723	0.9978	112.5	7	126.0 - 129.5°	—	—	4.0
2	72.0 - 97.0	1.5680	—	4.0	8	129.5 - 138.0	1.5976	—	6.5
3	97.0 - 106.5	1.5581	—	5.7	9	138.0 - 140.0	1.5947	1.0315	5.2
4	106.5 - 107.0	1.5514	0.9644	2.3	10	140.0 - 144.5	1.5895	—	1.8
5	107.0 - 108.0	1.5532	—	1.6	11	144.5 - 147.5	1.5860	—	4.0
6	108.0 - 126.0	1.5680	—	3.5	12	147.5 - 149.0	1.5855	—	1.0
					Residue				10.8

The literature data for 2-methyl-4-ethylaniline: b.p. 229 - 230°; melting point of the acetyl derivative 105 - 106° [21].

c) 7-Methylindole: Fraction No. 7 (4 g; b.p. 126 - 129.5° at 7 mm) contained a crystalline substance. After freezing out, filtering and washing with ether, 2.7 g of a substance with an m.p. of 78° was obtained. After recrystallization from water and sublimation, the substance melted at 85° and consisted of 7-methylindole.

Found %: C 82.35, 82.30; H 6.97, 6.89; N 10.48, 10.42. C_9H_9N. Calculated %: C 82.50; H 6.87; N 10.61.

A mixed sample with skatole and with α-methylindole displayed melting point depression: m.p. 75° and 58° respectively. 7-Methylindole picrate (from alcohol) consisted of red needles with an m.p. 176°.

Found %: N 15.73, 15.75. $C_{15}H_{12}O_7N_4$. Calculated %: N 15.54.

Literature data for 7-methylindole: b.p. 266°; m.p. 85°; 7-methylindole picrate: m.p. 176° [33].

SUMMARY

1. The dehydration of N-(β-hydroxyethyl)-aniline and N-(β-hydroxyethyl)-o-toluidine in the presence of aluminosilicates at 300° is complicated by dehydrogenation, hydrogenation and alkylation of the reaction products.

Aniline (the chief reaction product), 4-ethylaniline, indole, skatole and N,N'-diphenylpiperazine were isolated from the mixture of the products of the dehydration of N-(β-hydroxyethyl)-aniline. The presence of p-toluidine, N-ethylaniline, dihydroindole, 2,4-diethylaniline and quinaldine, and also of a mixture of di- and triethylindoles, was demonstrated by the preparation of crystalline derivatives.

2. o-Toluidine (the chief reaction product), 2-methyl-4-ethylaniline, and 7-methylindole were isolated from the product of the dehydration of N-(β-hydroxyethyl)-o-toluidine.

3. A scheme for the mechanism of the formation of the reaction products enumerated above was prepared.

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THE REACTION OF TRIETHYLSILANE WITH AMMONIA AND AMINES

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It was found in 1929 [1] that triphenylsilane reacts with a solution of sodium in liquid ammonia with formation of hexaphenyldisilazane:

$$2(C_6H_5)_3SiH + NaNH_2 \longrightarrow (C_6H_5)_3SiNHSi(C_6H_5)_3 + 2H_2.$$

Kraus and Nelson [2] subsequently found that triethylsilane reacts with an ammoniacal solution of potassium amide according to the scheme:

$$2(C_2H_5)_3SiH + KNH_2 \longrightarrow (C_2H_5)_3SiNKSi(C_2H_5)_3 + 2H_2.$$

Upon treatment with a solution of ammonium bromide in liquid ammonia, the potassium derivative is converted into hexaethyldisilazane.

The reaction of triphenylsilane [1, 3] and triethylsilane [2] with ethylamine in the presence of lithium which proceeds according to the following scheme, is also described in the literature:

$$R_3SiH + C_2H_5NH_2 \xrightarrow{Li} R_3SiNHC_2H_5 + H_2. \quad (R = C_6H_5,\ C_2H_5)$$

Lithium participates as a catalyst in this reaction; the rate of the reaction increases with increase in the concentration of lithium in the solution.

Gilman and co-workers [4] showed that triphenylsilane reacts with lithium dialkylamides according to the scheme:

$$(C_6H_5)_3SiH + LiNR_2 \longrightarrow LiH + (C_6H_5)_3SiNR_2.$$

The reaction of triethylsilane with ammonia and also with aliphatic, alicyclic and aromatic amines, both at ordinary and under increased pressure, was studied in the present work; it was shown under these conditions that triethylsilane reacts with ammonia in the presence of potassium amide even at − 35° with the formation of free hexaethyldisilazane, the yield of which amounts to 67 % of the theoretical. At the same time, triethylsilane does not react with ammonia at this temperature in the presence of sodium amide. Neither does triethylsilane react with ammonia in the absence of catalysts in an autoclave at 80 - 90°. The reaction of triethylsilane with ammonia could be brought about in the presence of lithium amide or sodium amide when it was carried out in an autoclave at temperatures of 20° and higher. Thus, for example, triethylsilane and ammonia in the presence of $LiNH_2$ at 20° forms 34% triethylaminosilane and 17% hexaethyldisilazane after 25 hours. In the presence of sodium amide, triethylsilane with ammonia forms 46% triethylaminosilane and 20% hexaethyldisilazane at 70° after 1 hour. It should be noted that sodium amide itself does not react with triethylsilane at 110°.

Thus, the reaction of triethylsilane with ammonia, which is catalyzed by the amides of the alkali metals, proceeds according to the scheme:

$$\begin{aligned} (C_2H_5)_3SiH + NH_3 &\xrightarrow{MNH_2} (C_2H_5)_3SiNH_2 + H_2; \\ (C_2H_5)_3SiH + (C_2H_5)_3SiNH_2 &\longrightarrow (C_2H_5)_3SiNHSi(C_2H_5)_3 + H_2. \end{aligned} \quad (M = K,\ Na,\ Li)$$

This scheme explains the increase in the yield of hexaethyldisilazane with increase in the atomic number of the alkali metal which is acting as the catalyst, since under these conditions, the rate of the reaction of triethylsilane with the amines [in the given case $(C_2H_5)_3SiNH_2$] increases. Another possible scheme for the formation of hexaethyldisilazane:

$$2(C_2H_5)_3SiNH_2 \longrightarrow (C_2H_5)_3SiNHSi(C_2H_5)_3 + NH_3.$$

appears to be less probable.

Primary aliphatic amines (ethylamine, n-propylamine) and aniline react smoothly with triethylsilane in the presence of the corresponding alkylamide of potassium, with the formation of triethyl(alkylamino)silanes in yields of 82 - 92%. Thus, for example, upon boiling triethylsilane with n-propylamine in which 2.5 mole%

of potassium is dissolved, when the reagents are taken in a molar ratio of 1:1.7, the theoretical quantity of hydrogen is evolved and 82.5% of triethyl-(n-propylamino)silane is formed. In the analogous reaction of triethylsilane with aniline, the yield of triethyl(phenylamino)silane amounts to 90%. On the other hand, in presence of sodium phenylamide triethylsilane does not react with aniline when boiled.

Primary aliphatic amines with secondary and tertiary alkyl radicals (isopropylamine, tert-butylamine, tert-amylamine, fenchylamine) and secondary aliphatic amines with primary alkyl radicals (diethylamine, di-n-butylamine, diisobutylamine) practically do not react with triethylsilane in the presence of the corresponding potassium amine derivative. However, when the reaction is carried out in an autoclave at 200 - 210°, the indicated amines react smoothly with triethylsilane with the formation of the corresponding triethyl(dialkylamino)silanes. Secondary amines with secondary radicals (dicyclohexylamine) do not react with triethylsilane even on heating for 13 hours in an autoclave at 240°.

The conditions of our experiments in which triethylsilane reacted with ammonia and amines are presented in Table 1. The physical properties of the 12 aminoderivatives of triethylsilane obtained by us, 8 of which were previously unknown, their analytical data and the molecular weight determinations are set forth in Table 2.

All the results obtained in the present work show that the reaction of triethylsilane with ammonia and amines is one of nucleophile substitution (type S_{N_2} of Ingold-Hughes) and can be represented by the following scheme:

$$RNH^{-} + (C_2H_5)_3SiH \longrightarrow [RNH\ldots(C_2H_5)_3Si\ldots H]^{-} \xrightarrow{RNH_2} RNHSi(C_2H_5)_3 + H_2 + RNH^{-}.$$

TABLE 1

Data on the Experiments Involving the Reaction of Triethylsilane with Ammonia and Amines

Initial amine		Catalyst metal	Ratio of reagents: R'R''NH: $(C_2H_5)_3SiH$: M	Temp. of reaction	Duration of reaction (hrs.)	Yield of end products of reaction (in%)	
R' =						Hydrogen	$R_3SiNR'R''$
H	H	–	12: 1	80 - 90°	6	0	0
H	H		15: 1: 0.4	20	20	100	34.3 + 17.1 $(C_2H_5)_3SiNHSi(C_2H_5)_3$
H	H	Na	19: 1: 0.1	−35 *	6	0	0
H	H	Na	15: 1: 0.04	70	1	100	20.4 + 45.9 $(C_2H_5)_3SiNHSi(C_2H_5)_3$
H	H	K	19: 1: 0.25	−35 *	8	100	66.8 $(C_2H_5)_3SiNHSi(C_2H_5)_3$
H	C_2H_5	K	2: 1: 0.03	80 - 100	2	100	91.2
H	n-C_3H_7	K	1.7: 1: 0.03	180 *	7	100	82.5
H	n-C_3H_7	K	1.7: 1: 0.08	105 *	8	0	0
H	n-C_3H_7	K	2: 1: 0.08	200 - 205	5	100	86.5
H	$C(CH_3)_3$	K	2.5: 1: 0.1	200 - 210	10	100	86.0
H	$CH(CH_3)_2$	K	1.9: 1: 0.1	200 *	7	50	43.8
	C_2H_5						
H	$C_{10}H_{17}$	K	1.4: 1: 0.07	200 - 210	9	100	80.4
H	C_6H_5	Na	2: 1: 0.04	110 *	4	0	0
H	C_6H_5	K	2: 1: 0.05	250 *	2	100	90.3
C_2H_5	C_2H_5	K	2: 1: 0.08	200 - 210	10.5	100	84.3
n-C_4H_9	n-C_4H_9	K	1.6: 1: 0.16	200 - 210	11	100	82.2
iso-C_4H_9	iso-C_4H_9	K	2: 1: 0.05	200 - 210	12	100	80.0
C_6H_{11}	C_6H_{11}	K	2: 1: 0.08	210 - 240	13	0	0

EXPERIMENTAL

Triethylsilane has a b.p. of 107.7° (760 mm); d_4^{20} 0.7309; n_D^{20} 1.4121.

The ammonia was evolved from a 30% aqueous solution, dried over solid KOH and collected in a trap, cooled to −80°. The amines were dried over solid KOH or over metallic sodium, after which they were fractionally distilled.

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* The reaction was conducted at ordinary pressure. The temperature indicated is the maximum temperature of the reaction mixture toward the end of the reaction.

TABLE 2

Physical Properties of the Triethyl(alkylamino)silanes $(C_2H_5)_3SiNHR$ and Triethyl(dialkylamino)silanes $(C_2H_5)_3SiNR_2$, Their Analytical Data and the Molecular Weight Determinations

Formula	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	γ^{20}	M		Silicon content (in %)	
							Calc'd	Found	Calc'd	Found
$(C_2H_5)_3SiNH_2$	137.2°	760	0.7990	1.4279	0.0083	23.10	131.29	128.7	21.38	21.19, 21.22
$(C_2H_5)_3SiNHC_2H_5$ *	170.3	760	0.7983	1.4290	0.0085	23.57	159.35	158.1 158.8	17.62	17.38, 17.56
$(C_2H_5)_3SiNHCH_2CH_2CH_3$ . . .	189.4	760	0.8038	1.4332	0.0086	24.19	173.37	171.8, 172.0	16.19	15.98, 16.03
$(C_2H_5)_3SiNHCH(CH_3)_2$	179.6	760	0.7962	1.4282	0.0085	22.95	173.37	171.0, 172.4	16.19	15.96, 16.01
$(C_2H_5)_3SiNHC(CH_3)_3$	193.4 - 193.8	760	0.8082	1.4360	0.0081	24.36	187.40	185.2, 185.3	14.99	14.79, 14.87
$(C_2H_5)_3SiNHC(CH_3)_2C_2H_5$ . . .	212 - 214	760	0.8194	1.4400	0.0086	25.50	201.42	199.2, 200.4	13.94	13.75, 13.77
$C_2H_5)_3SiNHC_{10}H_{17}$ **.	135.0	6	0.9035	1.4775	0.0085	29.14	267.52	264.1, 264.9	10.50	10.28, 10.34
$(C_2H_5)_3SiNHC_6H_5$ ***.	121.0 - 121.5	6	0.9336	1.5210	0.0163	31.89	207.39	205.4, 206.0	13.53	13.33, 13.41
$(C_2H_5)_3SiNHSi(C_2H_5)_3$	243.6 - 244.6	760	0.8461	1.4455	0.0088	25.71	245.56	243.3, 244.0	22.85	22.70, 22.71
$(C_2H_5)_3SiN(C_2H_5)_2$	200.5	760	0.8098	1.4400	0.0087	24.66	187.40	186.5, 187.3	14.99	14.75, 14.80
$(C_2H_5)_3SiN(n\text{-}C_4H_9)_2$	253.2 - 254.2	760	0.8280	1.4475	0.0087	26.33	243.50	242.9, 243.7	11.54	11.33, 11.37
$(C_2H_5)_3SiN(iso\text{-}C_4H_9)_2$	248 - 249.5	760	0.8318	1.4500	0.0084	29.85	243.50	240.6, 241.8	11.54	11.34, 11.39

* Literature data [9]: b.p. 63° (22 mm); d_4^{20} 0.7992; n_D^{20} 1.4290.

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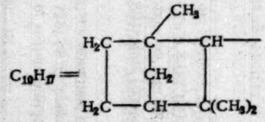

(fenchyl).

*** Literature data [9]: b.p. 130 - 132° (12 mm); d_4^{20} 0.9329; n_D^{20} 1.5210

The methods of the analysis and the determinations of the physical constants were analogous to those described in one of our previous works [5].

Reaction of triethylsilane with ammonia in the absence of catalysts. 11.6 g of triethylsilane and 25 ml of liquid ammonia were heated in an 0.25 liter steel autoclave at 80 - 90° for 6 hours. Hydrogen formation was not observed under these conditions and all the triethylsilane remained unchanged.

Reaction of triethylsilane with ammonia in the presence of sodium amide. a) 0.3 g of metallic sodium and 11.6 g of triethylsilane were added to 40 ml of liquid ammonia. The reaction mixture was stirred at − 35° for 6 hours. After evaporating off the ammonia, 10.5 g of the initial triethylsilane with a b.p. of 108.1° (760 mm) was isolated. b) 30 ml of liquid ammonia, 0.1 g of sodium and 11.6 g of triethylsilane were placed in a 0.25 liter steel autoclave which was cooled to − 65°. The autoclave was heated for 1 hour at 70°. In this period, pressure in the autoclave had risen to 40 atm. After cooling to room temperature, the pressure in the autoclave fell to 20 atm. 2.25 liters of hydrogen were evolved during the reaction and collected in a gasometer. By fractionally distilling the mixture, 6.0 g of triethylaminosilane with a b.p. of 137.5° at 767 mm (yield 45.9 % of the theoretical) and 5.0 g of hexaethyldisilazane with a b.p. of 244 - 245° (767 mm) were isolated. The physical constants of these compounds, which are set forth in Table 2, are in accord with the literature data.

The literature data for triethylaminosilane are [6]: b.p. 137.3°; n_D^{20} 1.4259 [7]. b.p. 134°, n_D^{20} 1.4267.

The literature data for hexaethyldisilazane [2] are: b.p. 100° (1 mm).

Reaction of triethylsilane with ammonia in the presence of potassium amide. 11.6 g of triethylsilane was added to a solution of 1.0 g of potassium in 40 ml of liquid ammonia. The reaction mixture was stirred at − 35° for 8 hours. The excess ammonia was evaporated off and the residue was fractionally distilled; 8.2 g of hexaethyldisilazane with a b.p. of 244.7° (760 mm) were thereby obtained. The yield was 66.8% of the theoretical.

Reaction of triethylsilane with ammonia in the presence of lithium amide. 30 ml of liquid ammonia, 11.6 g of triethylsilane and 0.3 g of lithium were placed in an 0.25 liter steel autoclave. The autoclave was left at room temperature (20°) for 20 hours. 2.4 liters of hydrogen was evolved as a result of the reaction. 4.5 g (34.3%) of triethylaminosilane with a b.p. of 137.5° at 759 mm and 4.2 g (51.1%) of hexaethyldisilazane with a b.p. of 243.5-244.5° (759 mm) were obtained by fractionally distilling the reaction mixture. Analogous results were obtained by replacing the lithium with 0.5 g of sodium.

Reaction of triethylsilane with sodium amide. 5 g of sodium amide, prepared by dissolving sodium in liquid ammonia [8]* and 11.6 g of triethylsilane were heated to 110° for 11 hours. No reaction was observed under these conditions; hydrogen was not evolved and all the triethylsilane remained unchanged. After redistillation it had a b.p. of 107-108° (758 mm); n_D^{20} 1.4120; d_4^{20} 0.7309.

Synthesis of triethyl(ethylamino)silane. 9.0 g of ethylamine (cooled to −80°), 11.6 g of triethylsilane and 0.1 g of potassium were heated in a 0.25 liter steel autoclave for 2 hours at 80-100°. 2.5 liters of hydrogen was evolved during the reaction and collected in a gasometer. 14.5 g (91.2%) of triethylaminosilane with a b.p. of 170.0° (754.4 mm) was obtained by fractionally distilling the reaction mixture. Its physical constants and analytical data are presented in Table 2.

The following were prepared in an analogous manner by reaction in an autoclave, but at 200-210°: triethyl-(isopropylamino)silane, triethyl(tert-butylamino)silane, triethyl(tert-amylamino)silane, triethyl(fenchylamino)-silane, triethyl(diethylamino)silane, triethyl(di-n-butylamino)silane and triethyl(diisobutylamino)silane. We did not succeed in obtaining all these compounds by the reaction of triethylsilane with the corresponding amines in the presence of the potassium amine derivative at ordinary pressure. The initial triethylsilane did not react in any of these cases.

Reaction of triethylsilane with dicyclohexylamine. 5.8 g of triethylsilane, 18.2 g of dicyclohexylamine and 0.3 g of potassium were heated in an autoclave at 240° for 13 hours. After this period, no further hydrogen evolution occurred. 5.2 g of unchanged triethylsilane and 17.8 g of dicyclohexylamine were isolated by fractionally distilling the reaction mixture.

Synthesis of triethyl(n-propylamino)silane. 0.1 g of finely divided potassium was dissolved by heating in 10.0 g of n-propylamine. 11.6 g of triethylsilane was added to the solution thus obtained. The reaction mixture was heated to boiling for 7 hours in a flask equipped with a reflux condenser, connected, via a Tishchenko bottle containing concentrated sulfuric acid, with a gasometer for collecting the hydrogen. At the end of this period, 2.5 liters of hydrogen had been evolved. By fractionally distilling the reaction mixture, 3.9 g of n-propylamine with a b.p. of 48.0-47.6° (752 mm) and 14.3 g of triethyl-n-propylaminosilane with a b.p. of 189.0° (751.9 mm) were obtained.

Triethyl(phenylamino)silane was obtained in an analogous fashion. Triethylsilane did not react with n-propylamine and aniline upon boiling in the presence of metallic sodium.

SUMMARY

The reaction of triethylsilane with ammonia and amines, which is catalyzed by the amides of the alkali metals, was studied. The dependence of the course of the reaction on the nature of the amine and catalyst was shown. The conditions for the synthesis of the amino, alkylamino and dialkylamino derivatives of triethylsilane with high yields were found. 12 compounds of this type were synthesized, 8 of which had been previously unknown, and their physical properties were determined.

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* To completely eliminate the ammonia, the sodium amide obtained was heated in a vacuum at 100° for two hours.

AZO DYES FROM 1,5-AMINONAPHTHOL AND CERTAIN OF ITS DERIVATIVES

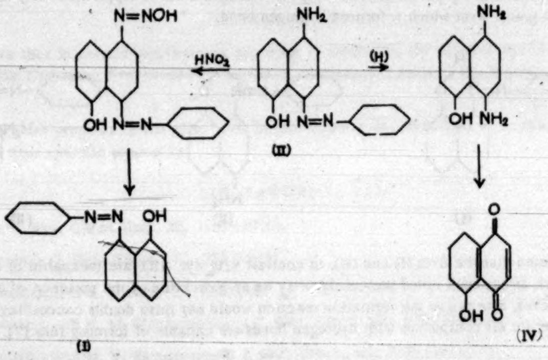
IX. THE HYDROGEN BOND IN CERTAIN PERI-HYDROXY AZO DYES

V. V. Perekalin and Z. S. Segalina

Ortho-hydroxy azo dyes of the naphthalenic series are markedly different in their properties from their isomeric peri-hydroxy azo dyes: in their insolubility or poor solubility in alkaline solutions, in the absence of absorption in the infra-red region which is characteristic of the hydroxy group and in the constant position of the long-wave maxima of the absorption curves during changes of the pH of the medium. The unusual behavior of the ortho-hydroxy azo dyes is to be explained in the light of the representations of tautomerism in the transition of the azoid form of the azo dye into the quinonhydrozone form. At the present time, the specific properties of ortho-hydroxy azo dyes are explained by the existence in them of an intramolecular hydrogen bond [1, 2, 3]. However, in spite of the fact that the hypothesis of hydrogen bonding apparently is in accord with reality, we can nevertheless formally assume tautomerism in the ortho-hydroxy azo dyes and ascribe a quinonhydrozone structure to them.

It is tempting to investigate the properties of those hydroxy azo dyes in which, on structural grounds, one can assume the existence of a hydrogen bond, but in which, on those same grounds, the possibility of azo-hydrozone tautomerism is restricted or entirely excluded. The peri-hydroxy azo dyes of the naphthalenic series are such compounds. In the first place is the simplest para-hydroxy azo dye: 8-benzeneazo-1-naphthol (I), and also 4-benzeneazo-1,5-aminonaphthol (II) and 1-benzeneazo-2,8-aminonaphthol (III).

8-Benzeneazo-1-naphthol (I) was synthesized for the first time from 4-benzeneazo-1,5-aminonaphthol after its diazotization and substitution with hydrogen of the diazo group formed. By combining 1,5-aminonaphthol with diazobenzene in a hydrochloric acid medium, an alkali-insoluble dye was isolated which proved to be not the ortho-hydroxyamino azo dye, but its para-hydroxy isomer—4-benzeneazo-1,5-aminonaphthol (II). Its structure was established by reduction to diaminonaphthol and oxidation of the latter into juglone (IV), which can be formed only if the initial dye was the peri-hydroxy-para-amino azo dye:



1-Benzeneazo-2,8-aminonaphthol (III) was prepared according to the preparative directions [4] from 2,8-aminonaphthol and diazobenzene in an acidic medium.

The peri-hydroxy azo dyes investigated by us (I, II and III) had a number of general properties. They were insoluble in alkalis; consequently, their hydroxy groups had considerably less acidic properties than those of the para-hydroxy isomers, which, as is well-known, dissolve readily in dilute alkaline solutions. Change in the pH of the medium did not influence the absorption curves; the position of the long wave maxima of these curves remained constant when the measurements were made in an alcoholic (1) and alcoholic-alkaline medium (2)

(Tables 1, 2 and the figure).*

It must be remembered that the conversion of the neutral molecules of the hydroxy azo dyes, when dissolved in alkalis, into their anions is accompanied by displacement of the position of the long-wave maxima in the visible region [5, 6]. Consequently, the investigated peri-hydroxy azo dyes were not converted by the action of alkali solutions into anions, their hydroxy groups did not react with sodium hydroxide and the hydrogen atoms of the hydroxy groups were without their usual lability.

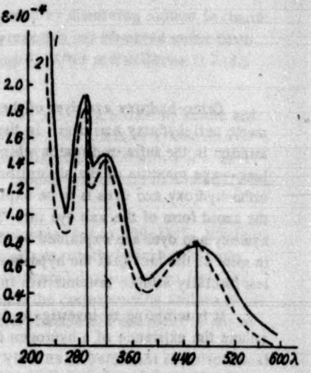


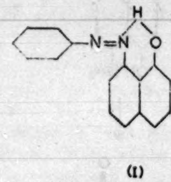
TABLE 1

Dye	λ, mμ	
	ethyl alcohol	ethyl alcohol + NaOH
8-Benzeneazo-1-naphthol	460	460
4-Benzene azo-1,5-aminonaphthol [6]	520	520
1-Benzeneazo-2,8-aminonaphthol [4]	500	500

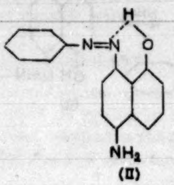
TABLE 2

Dye	Medium	Maxima					
		I		II		III	
		λ	ε	λ	ε	λ	ε
8-Benzene-azo-1-naphthol	ethyl alcohol	290	$1.86 \cdot 10^4$	320	$1.4 \cdot 10^4$	480	$0.775 \cdot 10^4$
	ethyl alcohol + NaOH	290	$1.89 \cdot 10^4$	320	$1.48 \cdot 10^4$	460	$0.76 \cdot 10^4$

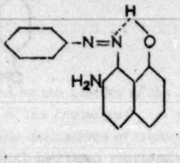
While we can formally use the representation of the slightly probable tautomeric conversion of the azoid form of the dye into the quinonhydrozone form (which does not contain the hydroxy group) to explain this unusually small lability of the hydrogen atoms of the hydroxy groups in the last two peri-hydroxy azo dyes (II and III), a similar conversion is impossible for the simplest para-hydroxy azo dye—8-benzeneazo-1-naphthol (I). Therefore, the lowering of the lability of the hydrogen atoms of the hydroxy groups in the peri-hydroxy azo dyes investigated can be explained by the assumption that the hydrogen atom is supplementarily linked with a nitrogen atom of the azo group, with which it forms a hydrogen bond.



(I)



(II)



(III)

It should be noted that the dyes (I) and (II), in contrast with dye (III), are incapable of forming laks (internal complex salts), which as has been noted previously, may be an indication of the presence of an intramolecular hydrogen bond; however, a negative lak formation reaction would not raise doubts concerning the existence of a hydrogen bond, since not all compounds with hydrogen bonds are capable of forming laks [7].

EXPERIMENTAL

1. Synthesis of 4-benzeneazo-1,5-aminonaphthol (II). 1.59 g of 1,5-aminonaphthol was ground with 1 ml of 37% hydrochloric acid solution and diluted to 200 ml with water (almost all the aminonaphthol went into the solution). 100 ml of an 0.1 N solution of diazobenzene, prepared according to the usual directions, was added over a period of 2 hours to a suspension of 1,5-aminonaphthol, which was being stirred and was at a temperature of 10°. As the diazo compound was added, the solution gradually became red colored and a precipitate of the dye began

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* The curves were taken on a SF-11 spectrophotometer by O. M. Dolzhanskaya, to whom we express our gratitude.

to separate from it. After the addition of all the diazo solution, the mixture was stirred for 5 hours more, left overnight and filtered. The dye in the form of a paste which had been washed with water, was triturated with 10 ml of 10% sodium hydroxide solution and diluted to 100 ml with water. The suspension, which had a weakly alkaline reaction, was heated to 50° for 5-10 minutes and filtered after cooling. The alkali-soluble azo dye, 2-benzene-1,5-aminonaphthol was isolated from the alkaline filtrate which had been acidified with dilute acetic acid. The precipitate was washed with water and again treated with alkali. Afaer recrystallization from ethyl alcohol, a finely crystalline brown dye – presumably 4-benzeneazo-1,5-aminonaphthol (II), m.p. 164-165° – was obtained. The dye was insoluble in dilute solutions of sodium hydroxide and dissolved in alcohol with an orange-red color, while in concentrated sulfuric acid it formed a blue solution, which gradually became violet. The yield was 0.42 g (16%).

Reduction of the dye. A saturated weakly alkaline aqueous solution of 1.5 g of hydrosulfite, heated to boiling, was gradually added to a boiling solution of 1 g of the dye in 50 ml of 90% ethyl alcohol; the color of the solution changed from orange-red to light yellow. The diaminonaphthol was not isolated from the solution after filtration, but was oxidized at once.

Oxidation of diaminonaphthol into juglone (IV). A 10% aqueous solution of ferric chloride was gradually added to a solution of 1,4-diamino-5-naphthol at a temperature of 5-7° and the color of the solution became dark red. The juglone which was formed was extracted with chloroform and after evaporating off the solvent, was purified by sublimation; it consisted of a dark brown powder, m.p. 144-147°, dissolved in a 10% solution of sodium hydroxide with a red coloration, which rapidly became brown, and formed a bright red solution in concentrated sulfuric acid.

2. Synthesis of 8-benzeneazo-1-naphthol (I). An equimolecular quantity of sodium nitrite in the form of a saturated solution was gradually added to a blue-violet solution of 1 g of 4-benzeneazo-1,5-aminonaphthol (II) in 50 ml of 95% ethyl alcohol, which was acidified with 2 ml of 96% sulfuric acid and heated to boiling; after the addition of all the sodium nitrite, the color of the solution became light brown. After distilling off some of the alcohol (15-20 ml) and cooling, the mixture was poured out into 100 ml of cold water, and the resinous precipitate was recrystallized from ethyl alcohol. 8-Benzeneazo-1-naphthol consisted of bronze-brown crystals, m.p. 90-92°; quite soluble in ethyl alcohol, insoluble in the cold and on heating with dilute and concentrated solutions of sodium hydroxide; the color of the dyeing with mordanted (with aluminum salts and chrome) and unmordanted wool was identical.

0.0980 g sub.: 0.2790 g CO_2; 0.0418 g H_2O. 0.0988 g sub.: 9.97 ml N_2 (23°, 753 ml). Found %: C 77.4; H 4.84; N 11.3. $C_{16}H_{12}ON_2$. Calculated %: C 77.5; H 4.79; N 11.6.

SUMMARY

1. It was shown that in certain peri-hydroxy azo dyes, in particular, the simplest dye of this series which was synthesized for the first time, 8-benzeneazo-1-naphthol, the hydrogen atom of the hydroxy group lacks its usual lability.

2. A hypothesis was proposed to the effect that in peri-hydroxy azo dyes there is an intramolecular hydrogen bond which explains their specific properties.

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* See Consultants Bureau Translation, page 985.

** See Consultants Bureau Translation, page 1451.

*** See Consultants Bureau Translation, page 141.

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CONCLUSIONS

1. [illegible]

2. [illegible]

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* See Consultants Bureau Translation, page 1461.

** See Consultants Bureau Translation, page 131.

SYNTHESIS OF SULFANILAMIDE DERIVATIVES IN THE LYSINE SERIES

M. N. Shchukina and Yuan-Chen-e

Lysine (α,ϵ-diaminocaproic acid) is one of the essential amino acids which has great significance for the processes of metabolism and growth in the organism. Its sulfanilyl-substituted derivatives are of undoubted interest for the investigation of their antibacterial action. Due to the two amino groups of lysine, it is possible to obtain the corresponding α- or ϵ-monosulfanilamide, and also the α,ϵ-disulfanilamide derivatives.

In spite of the fact that in diamino acids the aminogroup which is in the alpha position to the carboxyl group has a higher reactivity, the N^{α}-acetyllysine [1, 2] had not been successfully obtained by the direct acetylation of lysine even under mild conditions. Our experiments also confirmed this. We prepared the disulfanilamide derivative in low yield by the condensation of lysine with an equivalent quantity of p-acetylaminobenzensulfo chloride and isolated a very small quantity of N^{α}-(p-acetaminobenzensulfonyl)-lysinefrom the mother liquor. Therefore, in order to prepare the N^{α}- or N^{ϵ}-monosulfanilyl derivative, starting from lysine itself, it was necessary to preliminarily shield the α- or ϵ-amino group.

A method is described in the literature for shielding the ϵ-amino group by the formation of an oxazolidine ring from the carboxyl and α-amino group with the aid of the benzyl ester of chloroformic acid [3].

Racemic N^{α}-(p-aminobenzensulfonyl)-lysine was prepared by Adamson [4]; the ϵ-amino group was shielded by the formation of a homopiperidone ring by heating the methyl ester of lysine at 100°. In view of the low yield (below 10%), the method presents only theoretical interest.

A more convenient method of preparing N^{α}-sulfanylyl-substituted lysine was proposed by Kucherov and Ivanov [5], who prepared optically active N^{α}-(p-aminobenzensulfonyl)-lysines, starting with the corresponding N^{ϵ}-benzoyl derivatives of the lysines which are intermediate products in the isolation of lysine from casein. By the mild alkaline saponification of the N^{ϵ}-benzoyl-N^{α}-(p-acetylaminobenzen sulfonyl)-lysines, the N^{ϵ}-benzoyl bond is ruptured and the corresponding N^{α}-(p-aminobenzen sulfonyl)-lysines are formed. The biological properties of the substances obtained were not indicated.

There is a number of works in the literature involving the use of copper complexes of diamino acids in organic synthesis with the object of shielding the aminogroup [6, 7], but this method has not yet been used in syntheses of sulfanylamide derivatives. We succeeded in obtaining N^{α}- and N^{ϵ}-monosulfanilamide derivatives of d,l-lysine with the aid of its copper complex according to the scheme presented on the following page.

The N^{α},N^{ϵ}-bisacetylaminobenzen sulfonyl derivative was obtained by the condensation of lysine with excess p-acetylaminobenzensulfo chloride in an aqueous alkaline medium; its saponification with 15% hydrochloric acid led to N^{α},N^{ϵ}-bis-(p-aminobenzensulfonyl)-lysine. The action of concentrated sulfuric acid on the acetyl derivative in an alcohol medium led simultaneously to saponification and esterification.

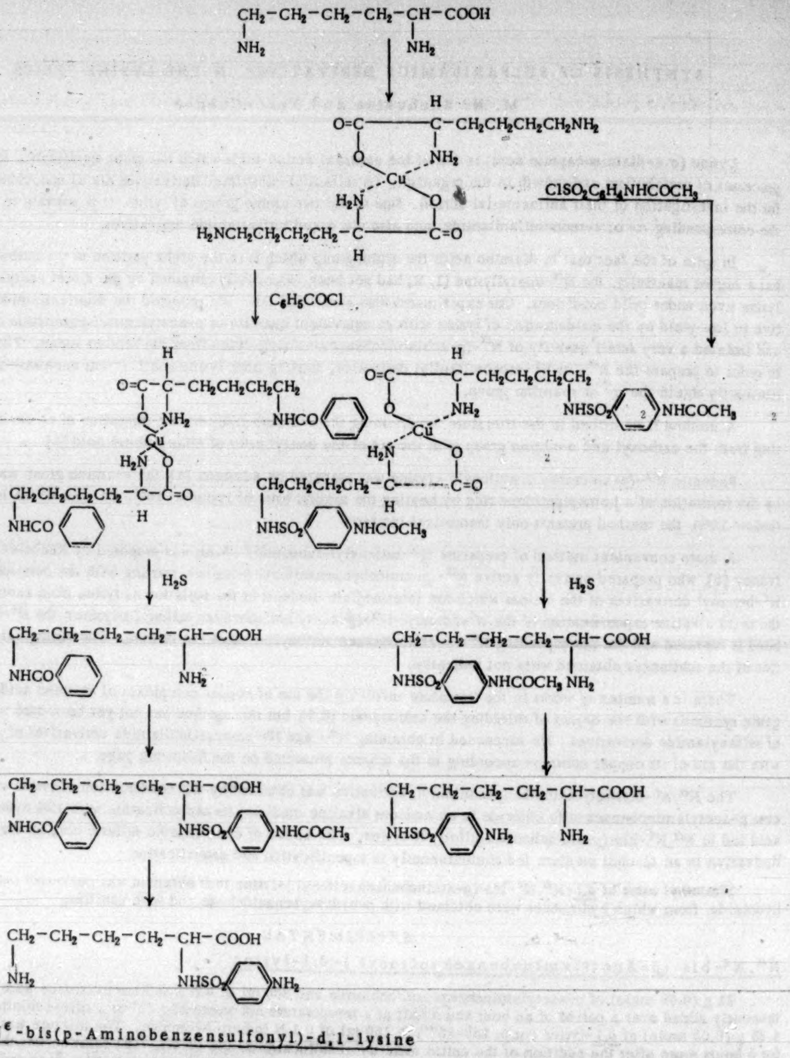
The ethyl ester of d,l-N^{α},N^{ϵ}-bis-(p-aminobenzen sulfonyl)-lysine thus obtained was converted into its hydrazide, from which hydrazones were obtained with p-hydroxybenzaldehyde and with vanillin.

EXPERIMENTAL

N^{α},N^{ϵ}-bis-(p-Acetylaminobenzen sulfonyl)-d,l-lysine

21 g (0.09 mole) of p-acetylaminobenzensulfochloride and 350 ml of 0.5 N sodium hydroxide were simultaneously added over a period of an hour and a half at a temperature not exceeding 35° to a stirred solution of 4.38 g (0.03 mole) of d,l-lysine (m.p. 255-257°) in 150 ml of 0.1 N sodium hydroxide. The mixture was stirred for 5 hours more after the addition of the entire quantity of sulfochloride and alkali. The solution was then filtered off from the unreacted sulfochloride and slowly acidified with concentrated hydrochloric acid (Congo red was the indicator) while it was being energetically stirred. The thick oil which precipitated gradually crystallized on standing for 2 days. The white precipitate obtained was filtered off and washed with 20 ml of water. 13.2 g of a substance with m.p. of 200-202° was obtained. The yield was 81.5% of the theoretical, calculating on the basis of the lysine taken. The substance did not give a blue color with ninhydrin, was quite soluble in 50% alcohol and difficultly soluble in cold water. Upon heating with water, even at 70-80°, the substance was partially decomposed with the evolution of acetic acid. After two-fold recrystallization from a twenty-fold quantity of 50% alcohol, the substance melted at 209-210°.

4,600 mg sub.: 0.432 ml N_2 (27°, 730 mm). 4.287 mg sub.: 3.613 mg $BaSO_4$: Found %: N 10.33; S 11.58. $C_{22}H_{28}O_8N_4S_2$. Calculated %: N 10.37; S 11.85.



N^{α}-N^{ϵ}-bis(p-Aminobenzensulfonyl)-d,l-lysine

A mixture of 12 g of the unpurified acetyl derivative (I) obtained above and 60 ml of 15% hydrochloric acid was heated on a boiling water bath for 1.5 hours. The hot solution was treated with carbon, filtered off and concentrated to dryness in a vacuum at 50-60°. The thick oil obtained was dissolved in 40 ml of water and decolorized with carbon. Sodium acetate was added to the transparent filtrate while it was being stirred until the acid reaction as indicated by Congo red disappeared. The oil which precipitated crystallized after several minutes. 8.5 g of unpurified substance (II) with a m.p. of 181.5-182.5° was obtained. The yield was 85% of the theoretical. After recrystallization from water, the m.p. was 183-184.5°.

7.503 mg sub.: 0.824 ml N_2 (25.5°, 733 mm). 5.933 mg sub.: 6.068 mg $BaSO_4$. Found %: N 12.13; S 14.05; $C_{18}H_{24}O_6N_4S_2$. Calculated %: N 12.28; S 14.04.

Ethyl Ester of N^{α}-N^{ϵ}-bis-(p-Aminobenzensulfonyl)-d,l-lysine

A solution of 4 g of (II) with a m.p. of 181-182° in 40 ml of anhydrous alcohol, saturated with hydrogen chloride, was left for several hours at room temperature. On the following day the reaction mass, in which the white precipitate was formed, was heated on a water bath for 2 hours and then concentrated in a vacuum and 50 ml of water was added to the residue. The solution obtained was decolorized with carbon and neutralized with sodium bicarbonate to disappearance of an acid reaction with Congo red as the indicator, and then a 10% solution of soda was added until the reaction was weakly alkaline to phenolphthalein. The oil which was evolved, crystallized. The precipitate was filtered off and washed with water. The yield was 3.6 g (85%). The ester obtained was very excellently soluble in alcohol, and poorly soluble in water. After two-fold recrystallization from alcohol, the substance had a constant m.p. of 130-131°.

5,704 mg sub.: 10.309 mg CO_2; 2.903 mg H_2O. 6.025 mg sub.: 0.625 ml N_2 (21.5°, 732 mm). Found %: C 49.32; H 5.69; N 11.60. $C_{20}H_{28}O_6N_4S_2$. Calculated %: C 49.59; H 5.78; N 11.57.

A mixture of 2 g of (I) (m.p. 200-202°), 12 ml of alcohol and 1.2 ml of concentrated sulfuric acid was heated on a water bath with a reflux condenser for 4 hours. On cooling to room temperature, a crystalline substance separated from the alcoholic solution. The mixture was poured out into 50 ml of 10% soda solution, which was cooled with ice. The brown oil which separated crystallized after standing for 2 hours. The precipitate obtained was dissolved in 25 ml of 5% hydrochloric acid to separate it from the acid-insoluble acetyl derivative. The acidic solution was treated with carbon and filtered off, after which soda was added until the reaction was alkaline to phenolphthalein. The colorless oil which separated crystallized on standing. The substance was washed with water and recrystallized from 5 ml of alcohol with carbon. The m.p. was 130-131°. The yield was 0.8 g.

Hydrazide of N^{α}-N^{ϵ}-bis-(p-Aminobenzensulfonyl)-d,l-lysine

1 ml of 85% hydrazine hydrate was added to a hot solution of 1.55 g of the ethyl ester (II) in 30 ml of 95% alcohol. The solution was boiled on a water bath and then the alcohol solution together with the small precipitate which formed was concentrated to dryness in a vacuum. The substance obtained was washed with 10 ml of alcohol to eliminate the excess hydrazine hydrate. 1.35 g of a substance with a m.p. of 209-212° was obtained. The hydrazide was poorly soluble in alcohol and in water. After recrystallization from 50% alcohol the m.p. was 217-218°.

3.245 mg sub.: 5.499 mg CO_2; 1.610 mg H_2O. 3.600 mg sub.: 0.555 ml N_2 (20°, 734 mm). Found %: C 46.25; H 5.55; N 17.34. $C_{18}H_{26}O_5N_6S_2$. Calculated %: C 46.00; H 5.53; N 17.87.

o-Hydroxybenzalhydrazide of N^{α}-N^{ϵ}-bis-(p-Aminobenzensulfonyl)d,l-lysine

1.3 ml of salicylic aldehyde was added to a solution of 0.5 g of the hydrazide (IV) (m.p. 217-218°) in 55 ml of hot 50% alcohol, and the mixture was heated for an hour and a half. On the following day the yellow precipitate which was formed was filtered off and washed with water, alcohol and ether. After recrystallization from 50% alcohol, in which it was very slightly soluble, the hydrazone had a m.p. of 156°.

3.026 mg sub.: 5.830 mg CO_2; 1.300 mg H_2O. Found %: C 52.58; H 4.80. $C_{25}H_{30}O_6N_6S_2$. Calculated %: C 52.26; H 5.23.

p-Hydroxy-m-methoxybenzalhydrazide of N^{α}-N^{ϵ}-bis-(p-Aminobenzensulfonyl)-d,l-lysine

A solution of 0.3 g of vanillin in 12 ml of alcohol was added to a hot solution of 1.2 g of the hydrazide (IV) in 140 ml of 50% alcohol. The mixture was heated on a water bath for an hour and a half. The solution was concentrated in a vacuum until a white precipitate appeared, which was filtered off and recrystallized from 50% alcohol. The m.p. was 143-146° and the weight 1.5 g.

N^{ϵ}-Benzoyl-d,l-lysine

12 g of copper carbonate was gradually added over a period of 15 minutes to a solution of 6 g of d,l-lysine in 180 ml of water, which was heated to 80° and stirred. The mixture was stirred for 15 minutes more and then the hot blue solution was filtered off from the unreacted copper salt; the precipitate was washed with small portions of water. After cooling, initially 3 ml of 40% sodium hydroxide and then, gradually, from a separatory funnel, 6 ml of freshly distilled benzoyl chloride over a period of 15 minutes, were added to the transparent filtrate after cooling, and while it was being energetically stirred. The alkalinity of the reaction mass was maintained by the addition of 6 ml of 40% sodium hydroxide (in 0.5 mm portions). A blue precipitate fell out, but the aqueous layer was still bluish in color. 1.5 ml more of benzoyl chloride and 2.5 ml of 40% sodium hydroxide were added, after which the aqueous layer became almost colorless. The stirring was continued for 12 hours. The blue precipitate of the

copper complex of N$^{\epsilon}$-benzoyl-d,l-lysine (14.8 g of the crude product) was filtered off and washed with a 5% solution of soda to eliminate the benzoic acid formed. The suspension of the copper complex obtained in 200 ml of 2% hydrochloric acid was saturated with hydrogen sulfide. The precipitate of cuprous sulfide formed was filtered off, the colorless filtrate was neutralized with a 40% solution of sodium hydroxide until the solution was no longer acid to Congo red (in the absence of a reaction which was alkaline to phenolphthalein); a white precipitate thereupon fell out which, after washing with water and recrystallization from 50% alcohol, had a decomposition temperature of 252-254°, which is in accord with the literature data for N$^{\epsilon}$-benzoyl-d,l-lysine [8, 9]. The substance obtained gave a blue color with ninhydrin, which indicates the presence of the free α-amino group. The yield was 3.2 g (31.2%), calculating on the basis of the lysine taken.

N$^{\alpha}$-(p-Acetylaminobenzen sulfonyl)-N$^{\epsilon}$-benzoyl-d,l-lysine

A mixture of 3.2 g of the benzoyl derivative (VII) and 65 ml of 0.1 N sodium hydroxide solution was stirred for 2 hours. A white paste thereupon formed, to which was added 5.9 g of p-acetylaminobenzensulfochloride and 105 ml of 0.5 N sodium hydroxide in order to keep the reaction mass alkaline to phenolphthalein. After 6 hours, almost all the sulfochloride dissolved. The unreacted sulfochloride was filtered off, and the filtrate was slowly rendered acidic to Congo red with hydrochloric acid while it was being energetically stirred. The oil which thereupon separated out, crystallized. The residue was filtered off, washed with cold water and dried. The substance obtained had a m.p. of 226-228°. The yield was 4.2 g (73.5%), calculating on the basis of the initial benzoyl derivative. The substance did not give a color with ninhydrin. The substance was recrystallized from 50% alcohol for analysis. It consisted of fine flakes, m.p. 227-229°.

7.056 mg sub.: 4.67 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: N 9.26. $C_{21}H_{25}O_6N_3S$. Calculated %: N 9.39.

N$^{\alpha}$-(p-Aminobenzensulfonyl)-d,l-lysine

A solution of 3.2 g of the acetyl derivative (VIII) (m.p. 226-228°) in 100 ml of 1 N sodium hydroxide was heated on a boiling water bath for 15 hours. After cooling, the solution was filtered off and the filtrate was acidified with concentrated hydrochloric acid (Congo red). The acidic solution was concentrated to dryness in a vacuum and the residue thrice extracted with 0.5 N hydrochloric acid in 33 ml portions. The combined extract was carefully neutralized with a concentrated solution of ammonia with litmus as the indicator. After two days, a precipitate fell out which did not melt at 300°. The yield was 1.2 g (56%), calculating on the basis of the acetyl derivative. The substance obtained, after recrystallization from 50 ml of water, decomposed at 280-282°, (according to Adamson [4], 286°).

3.342 mg sub.: 5.839 mg CO_2; 1.930 mg H_2O. 4.750 mg sub.: 0.598 ml N_2 (21°, 727 mm). Found %: C 47.67; H 6.46; N 13.99. $C_{12}H_{19}O_4N_3S$. Calculated %: C 48.00; H 6.33; N 14.00.

N$^{\epsilon}$-(p-Acetylaminobenzensulfonyl)-d,l-lysine

A solution of 12 g of d,l-lysine in 320 ml of water was heated to 80° while being stirred, and 24 g of copper carbonate was added to it over a period of 20 minutes, after which the mixture was stirred for 40 minutes more at 75-80°. The hot blue solution was filtered off, and to the blue filtrate after cooling was added initially 20 ml of 2 N sodium hydroxide and then 21 g of p-acetylaminobenzensulfochloride (10% excess) over a period of 20 minutes and while the solution was being stirred. The mixture was then stirred at room temperature for 15 hours; 30 ml more of 2 N sodium hydroxide was thereupon added in order to keep the reaction mixture consistently alkaline to phenolphthalein. After filtration, the blue precipitate (62 g of the crude product) was dissolved in 1 liter of 2% hydrochloric acid. Hydrogen sulfide was passed into the acidic solution of the copper complex obtained until the formation of cuprous sulfide ceased. Then the mixture was heated on a water bath at 70-80° for an hour and a half. After filtration from the cuprous sulfide, the solution was decolorized with carbon and concentrated to dryness in a vacuum. The substance obtained was twice recrystallized from 50% alcohol, for analysis. M.p. was 251-252°.

7.425 mg sub.: 0.817 ml N_2 (22°, 725 mm). Found %: N 12.14. $C_{14}H_{21}O_4N_3S$. Calculated %: N 12.24.

N$^{\epsilon}$-(p-Aminobenzensulfonyl)-d,l-lysine

The acetyl derivative obtained (X) was heated with 100 ml of 15% hydrochloric acid at 85-90° for 1.5 hours. The solution was then concentrated to dryness in a vacuum. The residue was dissolved in 150 ml of water and neutralized with a saturated solution of soda. The substance isolated (11.7 g) was recrystallized from 80 ml of 50% alcohol and 9.2 g (37.5%) calculating on the lysine) was obtained. The substance was once more recrystallized from a ten-fold quantity of 50% alcohol for analysis. The m.p. was 204-205° (with decomposition).

6.462 mg sub.: 0.804 ml N_2 (25.5°, 738 mm). Found %: N 13.83. $C_{12}H_{19}O_4N_3S$. Calculated %: N 14.00.

SUMMARY

1. The N^{α}- and N^{ε}-sulfanilyl-substituted d,l-lysines were synthesized via their copper complex.

2. N^{α},N^{ε}-disulfanilyl-substituted d,l-lysine and the corresponding ester, hydrazide and hydrazones were prepared.

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* See Consultants Bureau Translation, page 1185.

ALKAMINE ESTERS OF β-(4-HYDROXYPHENYL)-α-PHENYLPROPIONIC ACID

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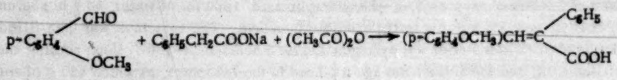
The valuable spasmolytic properties of the alkamine esters of diphenylacetic acid led to the introduction into practical medicine of the preparation "Trasentine" (spasmolytin) [1] and "Tropacine" [2]. The introduction into the aliphatic chain of a hydroxyl group and the conversion, thereby, into a series of benzilic acids, preserves the capacity of the diphenylmethane grouping to be the carrier of the valuable biological properties. Thus, the alkamine esters of benzilic acid [3] differ little in their spasmolytic action from the corresponding esters of diphenylacetic acid. We were interested in the question of the extent to which the bond of the two phenyl radicals with a single carbon atom was necessary for the alkamine ester to possess neurotropic activity.

The benzhydrylamine $(C_6H_5)_2CHNH_2$ is a highly active pharmacological substance and has anesthetic activity [4, a]. Its 3,3'-dipropylhydroxy derivative is 20 times more powerful as an anesthetic than novocain [4, 6]. 1,2-Diphenylethylamine $C_6H_5CH_2(C_6H_5)CHNH_2$ also possesses anesthetic activity and is a pharmacologically active substance [5]. One can conclude from a comparison of these compounds that α,β-diphenylpropionic acid also may serve as a carrier of neurotropic activity, while its alkamine esters can have a spasmolytic effect. If we consider the spasmolytic preparation as a heteropole in which there is, on the one hand, a basic group, for example, an aliphatic amine, and on the other hand, a group with an acidic character, then almost all spasmolytics fit in this scheme. A certain strengthening of the action of the phenyl group in such a heteropole via the introduction of a hydroxyl group into it may have been favorable for the spasmolytic effect. On the basis of these considerations, the alkamine esters of β-(4-hydroxyphenyl)-α-phenylpropionic acid, in which the heteropolar action of the phenyl groups is stretched out over the entire length of the propionic chain, served as the subject of the investigation.

β-(4-Hydroxyphenyl)-α-phenylpropionic acid was obtained for the first time [6] by the reduction with sodium of 4-hydroxy-α-phenylcinnamic acid, which, in turn, was prepared by boiling 4-hydroxybenzaldehyde with sodium phenylacetate in an acetic anhydride medium [7].

Since anisaldehyde is more accessible than 4-hydroxybenzaldehyde, it was more convenient for us to prepare β-(4-hydroxyphenyl)-α-phenylpropionic acid via the acrylic acid [8, 9]:



$$p\text{-}C_6H_4\begin{matrix}CHO\\OCH_3\end{matrix} + C_6H_5CH_2COONa + (CH_3CO)_2O \longrightarrow (p\text{-}C_6H_4OCH_3)CH{=}C\begin{matrix}C_6H_5\\COOH\end{matrix}$$

with subsequent hydrogenation and demethylation.

The condensation of anisaldehyde with sodium phenylacetate to form the corresponding acrylic acid is conducted with the aid of a 5-fold quantity of acetic anhydride at 170-180° [9]. It proved possible to make these conditions more mild: the acetic anhydride can be taken in an equimolecular quantity, calculating on the basis of the anisaldehyde; the temperature can be lowered to 100°, although this requires a certain lengthening of the condensation process.

For the conversion to the substituted propionic acid, the authors hydrogenated the sodium salt of β-(4-methoxyphenyl)-α-phenylacrylic acid in the presence of a porous nickel catalyst in an aqueous-alcoholic medium at 3 atm for 28 hours. The β-(4-methoxyphenyl)-α-phenylpropionic acid obtained by them had a m.p. of 105-107°. The yield was 93% of the theoretical. Faltis and others [10] carried out the hydrogenation with a palladium catalyst for 4 hours, and obtained acid with a m.p. of 120-121° after recrystallization from alcohol.

To demethylate the β-(4-methoxyphenyl)-α-phenylpropionic acid obtained, they heated it with a mixture of 48% hydrobromic acid and glacial acetic acid for 6.5 hours and obtained the hydroxy acid with a m.p. of 177-178° [9] in a yield of 88%. Bakunin [6] demethylated the acid with the aid of hydriodic acid and obtained a hydroxy acid with a m.p. of 177°.

We combined both processes in our work – that of hydrogenation and that of demethylation – replacing the acidic demethylation with an alkaline demethylation. The hydrogenation was carried out by us in an aqueous medium at 100°, while the demethylation was carried out at 220-225° with the aid of potassium hydroxide. The β-(4-hydroxyphenyl)-α-phenylpropionic acid which was obtained had a m.p. of 177°. The yield based on the initial methoxycinnamic acid was 94% of the theoretical.

We prepared the alkamine esters by two methods:

a) reaction of the acid chloride of the acid with the alkamine alcohol;

b) transesterification of the ethyl ester of β-(4-hydroxyphenyl)-α-phenylpropionic acid into the alkamine ester in the presence of a small quantity of metallic sodium.

The method of transesterification gives low yields of the esters, but in the method with the acid chloride we encountered the difficulty that during the action of thionyl chloride on β-(4-hydroxyphenyl)-α-phenylpropionic acid, a substance is formed which we could not isolate in the pure form; consequently, after the elimination of excess thionyl chloride from the reaction mass, the entire residue was introduced in the reaction with the alkamine alcohol.

The preparation proceeds considerably better if the phenol group is shielded with an acetyl radical. Then the pure acid chloride of β-(4-acetoxyphenyl)-α-phenylpropionic acid, with which the reaction of formation of the alkamine ester proceeds normally, can be isolated.

EXPERIMENTAL

β-(4-Methoxyphenyl)-α-phenylacrylic Acid

196 g of sodium phenylacetate (1.24 moles), 150 g of acetic anhydride (1.47 moles) and 195 g of commercial anisaldehyde which contained 81.5% of the pure aldehyde, were placed in a three-necked flask with a stirrer. The mixture was heated while being stirred for 45 hours at 100°. Upon cooling to 80°, 20 ml of water was carefully added, the mixture was left for 0.5 hour, and then 250 ml more of water was again carefully added. After stirring well and cooling, the precipitate which settled out was filtered off, washed with water and pressed out well. The precipitate was transferred to a dish, blended with 200 ml of methyl alcohol, filtered off again and once more washed with 200 ml of methyl alcohol. The acid filtered off was dissolved in 250 ml of 5% sodium carbonate solution, heated to boiling for 30 minutes with 10 g of carbon, filtered off from the carbon, and the filtrate was poured during stirring into 250 ml of 20% hydrochloric acid. The acid which precipitated after cooling was filtered off, washed with water and dried at 100°. 200 g (67.3%) of β-(4-methoxyphenyl)-α-phenylacrylic acid, calculating on the gasis of the anisaldehyde, was obtained and had a m.p. of 186-188°.*

β-(4-Hydroxyphenyl)-α-phenylpropionic Acid

300 g of β-(4-methoxyphenyl)-α-phenylacrylic acid, 1500 ml of water, 60 g of sodium hydroxide and 30 g of nickel catalyst were placed in a rotating 3-liter autoclave. The autoclave was then filled with hydrogen to a pressure of 60 atm. The material was hydrogenated for 4 hours at 90-100°. Upon cooling the autoclave, the catalyst was filtered off, and the filtrate was again placed in the autoclave, to which 420 g of sodium hydroxide was added. The autoclave was heated at 220° for 15-16 hours. The solution of the salt of β-(4-hydroxyphenyl)-α-phenylpropionic acid obtained was filtered and the filtrate was treated with hydrochloric acid until the reaction was acid. 270 g (94.4%) of a substance in the form of a fine white powder with a m.p. of 176-177° was obtained.**

Ethyl β-(4-Hydroxyphenyl)-α-phenylpropionate

A mixture of 6 g of β-(4-hydroxyphenyl)-α-phenylpropionic acid, 12 ml of anhydrous ethyl alcohol and 3 ml of concentrated sulfuric acid was heated on a water bath for 5 hours at the boiling point. Upon completion of the reaction, the mass was poured out into water. The precipitate which settled out was filtered off, washed with water, and then with 5% soda solution and again with water. After recrystallization from alcohol, 6.5 g (96%) with a m.p. of 77-78° was obtained. It consisted of white crystals, soluble in alcohol, ether, benzene and insoluble in water and soda.

3.06 mg sub.: 8.483 mg CO_2; 1.866 mg H_2O. Found %: C 75.48; H 6.81. $C_{17}H_{18}O_3$. Calculated %: C 75.55; H 6.66.

β-(4-Acetoxyphenyl)-α-phenylpropionic Acid

A mixture of 40 g of β-(4-hydroxyphenyl)-α-phenylpropionic acid, 50 g of acetic anhydride and 0.5 ml of concentrated sulfuric acid was heated at the boiling point with a reflux condenser for 7 hours. The reaction mass was then poured out into water. The oil which separated crystallized on standing. After recrystallization from 80% acetic acid, 35 g (74.5%) with a m.p. of 143-145° was obtained. The substance was soluble in alkali, acetone and hot acetic acid and was insoluble in water.

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* Ogliloro [8] indicates a m.p. of 188-189°; Baker and Sansbury [9], a m.p. of 186°.

** Bakunin [6] indicates a m.p. of 179-180°; Baker and Sansbury [9], a m.p. of 172-175°.

4.323 mg sub.: 11.340 mg CO_2; 2.094 mg H_2O. Found %: C 71.77; H 5.42. $C_{17}H_{16}O_4$. Calculated %: C 71.80; H 5.63.

Acid Chloride of β-(4-Acetoxyphenyl)-α-phenylpropionic Acid

A mixture of 10 g of β-(4-acetoxyphenyl)-α-phenylpropionic acid and 8.2 g of thionyl chloride was heated at 55-60° while being stirred, for 3 hours. After cooling, the reaction mass crystallized. The crystals were recrystallized from benzene.

The substance consisted of white needles with a m.p. of 91-93° (with decomposition). The yield was 9.5 g (90%).

The substance was soluble in benzene and ether and difficultly soluble in petroleum ether.

6.733 mg sub.: 2.300 mg AgCl. Found %: Cl 11.55. $C_{17}H_{15}O_3Cl$. Calculated %: Cl 11.73.

Acid Chloride of β-(4-Hydroxyphenyl)-α-phenylpropionic Acid

A solution of 10 g of β-(4-hydroxyphenyl)-α-phenylpropionic acid and 89.5 ml of 0.454 N alcoholic potassium hydroxide was concentrated to dryness in a vacuum. 10 g of thionylchloride was added to the dry residue. The mixture was heated for 1 hour at 50°; under these conditions the mass strongly effervesced. The excess thionyl chloride was then driven off in a vacuum. The residue, which was in the form of a hard brittle mass, could not be purified as a consequence of decomposition. It was converted into the amide.

Amide of β-(4-Hydroxyphenyl)-α-phenylpropionic Acid

The residue obtained above was stirred with 25 ml of 23% ammonia in methyl alcohol. The mixture was left for 48 hours. The crystals which formed were recrystallized from hot water.

The substance consisted of white crystals with a m.p. of 180-182°. The crystals were soluble in hot water and insoluble in cold water and alcohol.

6.588 mg sub.: 0.325 ml N_2 (19°, 728 mm). Found %: N 5.53. $C_{15}H_{15}O_2N$. Calculated %: N 5.80.

2-N,N-Dimethylaminoethyl β-(4-Hydroxyphenyl)-α-phenylpropionate

A solution of 0.4 g of metallic sodium in 20 g of dimethylaminoethanol was added to a solution of 5 g of ethyl β-(4-hydroxyphenyl)-α-phenylpropionate in 10 g of dimethylaminoethanol. The mixture was heated for 30 minutes, at 140°. 23 g of excess dimethylaminoethanol was then driven off in a vacuum. The residue was treated with dilute hydrochloric acid until the reaction was acid to Congo red and was extracted with ether. The ethereal extract was washed with a soda solution from which 2.4 g of β-(4-hydroxyphenyl)-α-phenylpropionic acid was isolated by acidification with hydrochloric acid.

0.5 g of ethyl β-(4-hydroxyphenyl)-α-phenylpropionate was obtained from the ethereal extract by driving off the ether.

The aqueous hydrochloric acid solution was neutralized with soda and then extracted with ether. After drying and driving off the ether, 1.5 g of dimethylaminoethyl β-(4-hydroxyphenyl)-α-phenylpropionate was obtained. The substance was recrystallized from alcohol: m.p. 115-116°. It was soluble in alcohol, hydrochloric acid and alkali and insoluble in soda solution and water.

7.585 mg sub.: 0.305 ml N_2 (25.5°, 729 mm). 5.335 mg sub.: 0.211 ml N_2 (25.5°, 729 mm). Found %: N 4.40, 4.34. $C_{19}H_{23}O_3N$. Calculated %: N 4.46.

Hydrochloride. The theoretical quantity of hydrogen chloride in anhydrous alcohol was added to the solution of base obtained. A white crystalline precipitate settled out with a m.p. of 150-152° (decomposition). It was quite soluble in water and insoluble in anhydrous alcohol and ether.

Found %: N 4.08. $C_{19}H_{23}O_3N \cdot HCl$. Calculated %: N 4.06.

Hydrobromide. The m.p. was 164-166° (with decomposition). It was soluble in water and insoluble in anhydrous alcohol and ether.

8.165 mg sub.: 0.273 ml N_2 (24.5°, 730 mm). 2.646 mg sub.: 1.283 mg AgBr. Found %: N 3.68; Br 20.60. $C_{19}H_{23}O_3N \cdot HBr$. Calculated %: N 3.57; Br 20.29.

2-N,N-Diethylaminoethyl β-(4-Hydroxyphenyl)-α-phenylpropionate

A solution of 10 g of β-(4-hydroxyphenyl)-α-phenylpropionic acid in 89.5 ml of 0.454 N alcoholic potassium hydroxide was concentrated to dryness in a vacuum. 10 g of thionyl chloride in 10 ml of dry benzene was added to the dry residue. The mixture was heated at 50° for 1 hour; under these conditions the mass strongly foamed. The excess of thionyl chloride was then driven off in a vacuum. Benzene and 20 ml of diethylaminoethanol were then added to the residue, which had the form of a hard, brittle mass. The reaction mixture was stirred and heated for 4 hours at the boiling point. The benzene and diethylaminoethanol were then driven off in a vacuum. The residue was diluted with water, neutralized with soda solution and extracted with ether. 2 g of the initial acid was recovered from the soda solution. The hydrochloride, which solidified with difficulty, was isolated from the ethereal extract after drying over anhydrous sodium sulfate and adding an alcoholic solution of hydrogen chloride; it was recrystallized from acetone. The yield was 4 g; m.p. 127-129° (with decomposition). It was quite soluble in water and hot acetone and was insoluble in anhydrous alcohol and ether.

9.395 mg sub.: 0.277 ml N_2 (28.5°, 720 mm). 3.378 mg sub.: 1.305 mg AgCl. Found %: N 3.58; Cl 9.56. $C_{21}H_{27}O_3N \cdot HCl$. Calculated %: N 3.71; Cl 9.40.

Hydrobromide. The m.p. was 139-141° (decomposition). It was soluble in water and hot acetone and insoluble in anhydrous ether and alcohol.

8.420 mg sub.: 0.258 ml N_2 (27.5°, 727 mm). 3.796 mg sub.: 1.697 mg AgBr. Found %: N 3.32; Br 19.02. $C_{21}H_{27}O_3N \cdot HBr$. Calculated %: N 3.31; Br 19.94.

The isolated base had a m.p. of 65-66°. It was insoluble in water and soluble in ether, alcohol and other organic solvents.

5.335 mg sub.: 0.211 ml N_2 (25.5°, 729 mm): Found %: N 4.34. $C_{21}H_{27}O_3N$. Calculated %: N 4.10.

3-N,N-Dimethylaminopropyl β-(4-Hydroxyphenyl)-α-phenylpropionate

It was prepared from 5 g of ethyl β-(4-hydroxyphenyl)-α-phenylpropionate and 10 g of dimethylaminopropanol analogously to the dimethylaminoethyl ester. After drying and distilling off the ester, 0.7 g of the base, which could not be crystallized and purified, was obtained. It was dissolved in ethyl acetate and neutralized with a solution of hydrogen chloride in anhydrous ether. The hydrochloride which precipitated was recrystallized from ethyl acetate. The m.p. was 140-141° (with decomposition).

7.100 mg sub.: 0.245 ml N_2 (22°, 734 mm). 8.335 mg sub.: 0.287 ml N_2 (22°, 734 mm). Found %: N 3.91, 3.85; $C_{20}H_{25}O_3N \cdot HCl$. Calculated %: N 3.87.

3-N,N-Diethylaminopropyl β-(4-Hydroxyphenyl)-α-phenylpropionate

It was prepared from 5 g of the ethyl β-(4-hydroxyphenyl)-α-phenylpropionate and 12 g of 3-diethylaminopropanol analogously to the preceding. The base isolated from the alkamine ester did not crystallize. It was dissolved in ethyl acetate and neutralized with a solution of hydrogen bromide and anhydrous alcohol. The hydrobromide crystallized out on prolonged standing. After recrystallization from ethyl acetate, the m.p. was 134° (with decomposition). It consisted of a crystalline substance, quite soluble in water and hot ethyl acetate and insoluble in anhydrous alcohol and ether.

8.885 mg sub.: 0.265 ml N_2 (24°, 732 mm). 6.480 mg sub.: 0.190 ml N_2 (24°, 732 mm). 4.912 mg sub.: 2.134 mg AgBr. Found %: N 3.30, 3.25; Br 18.49. $C_{22}H_{29}O_3N \cdot HBr$. Calculated %: N 3.21; Br 18.33.

2-N,N-Diethylaminoethyl β-(4-Acetoxyphenyl)-α-phenylpropionate

4 g of diethylaminoethanol was added to a stirred solution of 9.7 g of the acid chloride of β-(4-acetoxyphenyl)-α-phenylpropionic acid in 25 ml of dry toluene. The mixture was heated for 4 hours at the boiling point of toluene. After cooling, dilute hydrochloric acid was added to the reaction mass.

2 g of the initial acid was isolated from the toluene layer after drying and distillation. The acidic layer was neutralized with a 5% solution of alkali and extracted with ether. After drying and driving off the ether, 8.5 g of the base was isolated in the form of a thick oil. It was dissolved in ethyl acetate and treated with an alcoholic solution of hydrogen bromide. The hydrobromide which was isolated after recrystallization from ethyl acetate had a m.p. of 134-135° (decomposition). It consisted of a white crystalline substance, which was quite soluble in water and hot ethylate; it was insoluble in ether.

9.355 mg sub.: 0.260 ml N_2 (24°, 736 mm). 8.413 mg sub.: 0.237 ml N_2 (25°, 733 mm). Found %: N 3.09, 311. $C_{23}H_{29}O_4N \cdot HBr$. Calculated %: N 3.08.

The hydrochloride, recrystallized from ethyl acetate, had a m.p. of 127° (with decomposition).

7.915 mg sub.: 0.261 ml N_2 (30°, 733 mm). 8.150 mg sub.: 0.262 ml N_2 (30°, 735 mm). 14.318 mg sub.: 1.77 ml $AgNO_3$. 14.318 mg sub.: 1.77 ml $AgNO_3$. Found %: N 3.57, 3.49; Cl 8.96, 8.77. $C_{23}H_{29}O_4N \cdot HCl$. Calculated %: N 3.33; Cl 8.46.

SUMMARY

The dimethylaminoethyl, diethylaminoethyl, dimethylaminopropyl and diethylaminopropyl esters of β-(4-hydroxyphenyl)-α-phenylpropionic acid, and also the diethylaminoethyl ester of β-(4-acetoxyphenyl)-α-phenylpropionic acid and other compounds were synthesized.

The specified esters may have valuable biological properties.

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SYNTHESIS OF p-NITRO-o-ANISIDINE VIA DIARYLUREA AND ITS DINITRO DERIVATIVE

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p-Nitro-o-anisidine (2-methoxy-4-nitroaniline) or, as it is called in technology, azoamine rose O, appears in the aniline dye industry as an intermediate product in the preparation of synthetic insoluble azo dyes on the fiber. A method worked out by Soviet authors [1] for nitrating the N-arylsulfonyl derivative of o-anisidine with 10% dilute nitric acid with heating to 80° lies at the base of its industrial preparation.

The starting material for the preparation of p-nitro-o-anisidine is o-anisidine, which undergoes alkylation and nitration with subsequent hydrolysis of the nitro-derivative.

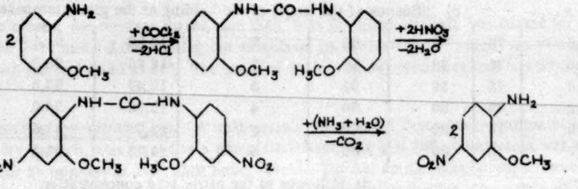
p-Toluenesulfochloride is used as the acylating agent.

The use of p-toluenesulfochloride as the acylating agent makes the production considerably more expensive in comparison with processes in which, for example, acetic or formic acid is used as the acylating agent.

In addition, the last phase of the process – the hydrolysis of arylsulfonnitroanilide with 80% sulfuric acid at 135-150° or with concentrated sulfuric acid in the cold – presents certain difficulties, since it is accompanied by side reactions; sulfonation, the formation of sulfones and resinification.

In view of this, we worked out a new method for preparing p-nitro-o-anisidine via diarylurea and its dinitro derivative. The cheap and quite accessible phosgene is used as the acylating agent in this case.

The acylation of o-anisidine with phosgene proceeds readily with the formation of 2,2'-dimethoxydiphenylurea; upon nitration of the latter with nitric acid, 4,4'-dinitro-2,2'-dimethoxydiphenylurea is formed; p-nitro-o-anisidine is obtained by its hydrolysis under appropriate conditions:



We phosgenated o-anisidine in an aqueous medium at 40°; the yield of 2,2'-dimethoxydiphenylurea amounted to 98.5-98.8% of the theoretical.

2,2'-Dimethoxydiphenylurea was nitrated with weak nitric acid in an aqueous suspension at high temperature, which resulted in the formation chiefly of 4,4'-dinitro-2,2'-dimethoxydiphenylurea and only in very insignificant quantity of the isomeric 6,6'-dinitro-2,2'-dimethoxydiphenylurea. 5,5'-Dinitro-2,2'-dimethoxydiphenylurea was not formed at all [2].

4,4'-Dinitro-2,2'-dimethoxydiphenylurea was obtained in a yield of 92.1-93.2% of the theoretical as a result of the nitration of 2,2'-dimethoxydiphenylurea by this method.

The last stage of the process is the hydrolysis of 4,4'-dinitro-2,2'-dimethoxydiphenylurea.

There are indications in the literature [3] to the effect that the hydrolysis of diphenylurea and its substituted derivatives proceeds better in an alcoholic ammonia solution heated under pressure. Gershzon and Lastovsky [4] found that di-o-tolylurea, which is slightly changed by treatment with acid or alkali at ordinary pressure, is almost completely hydrolytically decomposed in an acidic medium under increased pressure.

In preceding works [5] we have studied in detail the hydrolysis of diphenylurea and its dinitro-derivative, both in acidic and in alkaline media and have shown that an aqueous ammonia solution is a better hydrolyzing agent. The indicated ureas are almost completely hydrolyzed in a dilute ammonia solution at 150° under increased pressure, and the reaction products obtained as a result have a melting point which is very close to that indicated in the literature. These data are completely confirmed in the present work.

Our experiments showed that the hydrolysis of 4,4'-dinitro-2,2'-dimethoxydiphenylurea in a medium of 1% aqueous ammonia at 150° and under increased pressure, proceeds very readily and yields 2-methoxy-4-nitroaniline in a yield above 90% of the theoretical.

TABLE 1

Expt. No.	Amount		Nitric acid concentration (%)	Temperature	Length of time held at the given temperature	Experimental results		
	2,2'-dimethoxydiphenylurea (g)	nitric acid (ml)				yield (g)	yield (%)	melting point of the product
				a) Influence of the quantity of nitric acid				
1	10	150	30	80°	3	11.99	89.5	268°
2	10	100	30	80	3	11.90	88.8	273.5
3	10	75	30	80	3	12.10	90.3	269
4	10	75	30	80	3	12.40	93.0	270
5	10	50	30	80	3	12.26	91.5	267
				b) Influence of the nitration temperature				
6	10	75	30	100	3	11.05	82.4	273.5
7	10	75	30	95	3	11.75	87.4	272
8	10	75	30	90	3	11.78	87.9	272
9	10	75	30	80	3	12.21	91.3	269
10	10	75	30	80	3	12.30	92.4	270
11	10	75	30	70	3	12.1	90.3	265
				c) Influence of the length of the holding at the given temperature				
12	10	75	30	80	2	12.22	91.1	268
13	10	75	30	80	3	12.60	93.3	271
14	10	75	30	80	3	12.49	93.5	270
15	10	75	30	80	4	12.09	90.2	269
16	10	75	30	80	6	11.75	87.6	272
17	10	75	30	80	8	11.73	87.5	270
				d) Influence of the nitric acid concentration				
18	10	75	40	80	3	11.85	88.4	265
19	10	75	30	80	3	11.93	89.0	270
20	10	75	20	80	3	12.08	90.1	270
21	10	75	15	80	3	12.50	93.2	268
22	10	75	15	80	3	12.48	93.1	265
23	10	75	10	80	3	12.00	89.5	260
24	30	225	15	80	3	36.75	91.8	275

Hydrolysis in a pure water medium, without addition of ammonia, also gives a high yield of the end product, but it is qualitatively poorer, since some resinification occurs in this case.

The quality of the p-nitro-o-anisidine is considerably improved by purifying the crude product with the aid of sulfuric acid; the losses during this purification amount to about 3%.

We assume, however, that the necessity for such purification may be eliminated, if the end product is isolated not in the form of azoamine, but in the form of its stable diazo compound; the synthesis of p-nitro-o-anisidine via diarylurea and its dinitro-derivative would then be still simpler.

EXPERIMENTAL

Phosgenation of o-anisidine. 30.8 g of o-anisidine and 250 ml of water were placed in a 600 ml four-necked flask, equipped with a stirrer, thermometer, inlet tube for phosgene and outflow tube for the outgoing gases, and then 12.4 g of gaseous phosgene was introduced into the stirred liquid at 25° over a period of 30 minutes. The reaction medium was kept weakly alkaline during the phosgenation by periodic addition of sodium bicarbonate solution. Upon completion of the passage of phosgene, the reaction mixture was stirred for 15 minutes, after which air was blown through to eliminate the excess phsogene and the mixture was filtered. The filtered product was washed several times with weak hydrochloric acid, pressed out well and dried at 60-80°. The dry crystalline product had a light grey color.

A total of about 1% of o-anisidine which had not reacted was contained in the filtrate and the wash water. The yield of 2,2'-dimethoxydiphenylurea was 98.5-98.8% of the theoretical; the m.p. was 183°. After recrystallization from chlorobenzene, the m.p. was 185-185.5°, which was in accord with that indicated in the literature.

Nitration of 2,2'-dimethoxydiphenylurea. Nitric acid was introduced into a 200 ml three-necked flask equipped with a stirrer, a thermometer and a reflux condenser, and while the stirrer was going, a paste of 2,2'-dimethoxydiphenylurea in a quantity which was equivalent to 10 g of the dry substance with a m.p. of 183-185°, was placed in the flask. The mixture was heated to 80° and held at this temperature for 3 hours. Insignificant quantities of the anti-foaming agent acidol or the anti-foaming agent OP-7 and OP-10 (by-products of the soap industry) were added in separate experiments. The mixture was then cooled to 40-45° and filtered off. The 4,4'-dinitro-2,2'-dimethoxydiphenylurea was washed with cold water until the wash water was no longer acid to Congo red, was pressed out well and dried at 100°.

The influence of the quantity and concentration of the nitric acid, the influence of the temperature and the duration of the reaction (at 80°) are presented in Table 1.

4,4'-Dinitro-2,2'-dimethoxydiphenylurea was purified with the aid of glacial acetic acid and chlorobenzene; the m.p. was 280° (in bulk).

Hydrolysis of 4,4'-dinitro-2,2'-dimethoxydiphenylurea. 36.2 g of 4,4'-dinitro-2,2'-dimethoxydiphenylurea (0.1 mole) in the form of a paste and as much aqueous ammonia solution as was necessary for the total ammonia concentration (taking into account the water included in the paste) to amount to 7%, while its quantity was 1,000 ml, were placed in a 8-liter, enameled autoclave equipped with an ammonia manometer, a stirrer and a socket for the thermometer.

The autoclave was closed, the mixture stirred, and then, with the stirrer stopped, was heated for 3 hours at 150°; the pressure reached 9-10 mm. After cooling the autoclave, its contents were filtered; the precipitate was washed with water, pressed out and dried at 80°. The yield of dry 2-methoxy-4-nitroaniline was 28.3 g (84%); the m.p. was 136-137°.

Purification of 2-methoxy-4-nitroaniline. A well-pressed-out paste of 2-methoxy-4-nitroaniline, which contained 28.3 g of the dry product, was placed in a porcelain beaker, 220 g of 35% sulfuric acid was added and the mixture was heated for 20 minutes at 100° while being stirred. The hot acidic solution was filtered and about 150 ml of water was preliminarily poured into the suction flask. The insoluble residue was washed on the filter with hot water (2 times with 50 ml portions). The purified 2-methoxy-4-nitroaniline, which precipitated from the cooled filtrate, was filtered off, washed with cold water until the wash water no longer had an acid reaction, and was dried at 80° The weight of the dry 2-methoxy-4-nitroaniline was 27.15 g (80.6%); m.p. 139-140°.

TABLE 2

Expt. No.	Amount		Concentration of the aqueous ammonia solution (%)	Experimental results					
	dinitro product (g)	aqueous ammonia solution (ml)		yield		m.p. of the product	yield of the final product after purification		m.p. of the final product
				(g)	(%)		(g)	(%)	
1	36.2	1000	7	28.3	84.0	136°	27.15	80.6	139°
2	30	900	4.5	23.66	84.2	136.5	22.5	80.7	139.5
3	30	900	1	25.85	90.1	135	24.69	86.6	139
4	20	800	1	17.7	93.0	134.5	16.96	90.2	138
5	30	900	9	22.3	80.2	137	21.86	78.6	140

The results obtained in the experiments with aqueous ammonia solutions of various concentrations, are presented in Table 2.

4,4'-Dinitro-2,2'-dimethoxydiphenylurea was hydrolyzed in an aqueous medium in the same autoclave. 161 g of 4,4'-dinitro-2,2'-dimethoxydiphenylurea in the form of a paste (50 g of the dry product) and 389 ml of water were placed in an autoclave so that the total quantity amounted to 500 ml. The mixture was heated to 160° while being stirred and held at this temperature for 3 hours. The maximum yield of 2-methoxy-4-nitroaniline was 91.4% of the theoretical (m.p. 130°). After purification by dissolving it in 10% hydrochloric acid and precipitation with calcined soda, the yield of 2-methoxy-4-nitroaniline amounted to 86% (m.p. 135°).

SUMMARY

1. A new method proposed by us for the synthesis of 2-methoxy-4-nitroaniline via the diarylurea and its dinitro-derivative has advantages over the method currently used in industry.

2. The treatment of o-anisidine with phosgene readily leads to the formation of 2,2'-dimethoxydiphenylurea.

3. The method of preparing the dinitro-derivatives of diphenylurea by the action of dilute nitric acid at increased temperature was also found entirely applicable for the nitration of 2,2'-dimethoxydiphenylurea.

4. The hydrolysis of 4,4'-dinitro-2,2'-dimethoxydiphenylurea proceeds readily in a 1% aqueous solution of ammonia at increased temperature and pressure.

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* See Consultants Bureau Translation, page 1419.

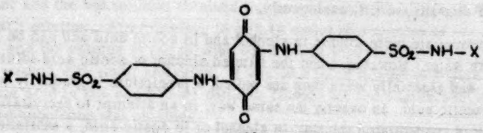
** See Consultants Bureau Translation, pages 1637, 2259.

INVESTIGATION IN THE FIELD OF QUINONES

VIII [1]. CONDENSATION OF p-BENZOQUINONE WITH SULFANILAMIDES

I. S. Ioffe, N. A. Filippova and Z. Ya. Khavin

In 1946 Postovsky and Pushkareva [2] described the products of the condensation of p-benzoquinone and chloranil with sulfanilamide and with sulfanilacetamide, which contain, joined with the quinoid nucleus, 2 sulfanilamide radicals, of the general type (I):



(1)

In developing this work, we condensed p-benzoquinone with sulfapyridine, sulfathiazole and sulfapyrimidine and thereby obtained the correspondingly amino group-substituted derivatives of the disulfanilamidoquinone type (I).

Like unsubstituted disulfanilamidoquinone, all the substances obtained were insoluble in water and in ordinary organic solvents. They melt above 300°. For purification we subsequently boiled the reaction products with alcohol and with acetic acid until colorless filtrates were obtained. To analyze them for sulfur content, we used the method of oxidizing with permanganate in an alkaline solution with subsequent reduction of the excess permanganate with hydrochloric acid and precipitation of the sulfate ion in the form of barium sulfate. This method, among other things, is entirely applicable for the analysis of various sulfanilamides.

The disulfanilamidoquinones were soluble in dilute aqueous solutions of caustic alkalis, but were not dissolved even in 10% soda. The alkaline solutions of the disulfanilamidoquinones were brown colored, and upon acidification, unchanged disulfanilamidoquinones were recovered from them. Reprecipitation from alkali is also applicable for purifying these substances.

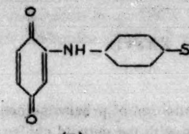
However, when alkaline solutions of the sulfanilamidoquinones are kept for a long time, the latter, even at room temperature, are slowly decomposed. Thus, for example, when 1 g of distreptocidoquinone was dissolved in 200 ml of 0.1 N NaOH and the solution obtained was acidified, 0.8 g of unchanged starting material was recovered after keeping the solution at room temperature for 4 hours; but after keeping such a solution for several days no precipitate of distreptocidoquinone whatever was isolated upon acidification. Distreptocidoquinone is least stable in alkaline solutions. The presence, in the amide groups of the sulfanilamidoquinones, of heterocyclic radicals increases their stability to alkalis. The most stable is disulfapyrimidinoquinone.

In view of the practical insolubility of the disulfanilamidoquinones, we decided to prepare the hitherto unknown monosulfanilamidoquinones, expecting that they would be distinguished by a better solubility in organic solvents.

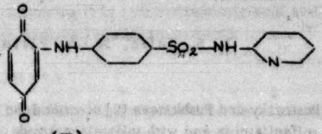
Diamino derivatives are ordinarily formed by the reaction of p-benzoquinone with amino compounds. However, diverse monoaminoquinones have been described in the literature, for example, monoanilinoquinone [3, 4] and mono-(methylamino)-quinone [4]; we have prepared monoglycinoquinone and monoalaninoquinone [5].

There are indications [3] that it is easier to stop the reaction at the monoaminoquinone stage when slightly active amines are acting on the quinone. We assumed that the formation of monoaminoquinones must be facilitated by the presence in the reaction medium of excess quinone, and the conduct of the reaction under conditions in which the monoamino derivative settles out as a precipitate as it is formed. On these grounds, we carried out the reaction of p-benzoquinone with sulfanilamide in a dilute aqueous solution in the presence of sodium chloride at ordinary temperature and introduced a considerable excess of quinone (from 6 to 10 moles per mole of amine) into the reaction. The gradual settling out of a reddish-brown flocculent precipitate, which consisted of a mixture of disulfanilamidoquinone and monosulfanilamidoquinone with a considerable predominance of the latter, was thereupon observed.

We treated the mixture obtained with boiling alcohol to separate the monosulfanilamidoquinone, filtered the solution from the alcohol-insoluble distreptocidoquinone and then diluted the alcoholic solution with water and thus isolated the monostreptocidoquinone (II):



(II)



(III)

We prepared monosulfidinoquinone (III) analogously.

Monosulfanilamidoquinones are quite soluble in alcohol and in acetic acid and can be isolated from these solvents by precipitation with water. However, when the filtered alcohol or acetic acid solutions of monosulfanilamidoquinone are let stand, and especially when they are boiled, a precipitate is gradually formed which is still insoluble in alcohol and in acetic acid. In exactly the same way, in an attempt to recrystallize monosulfanilamidoquinone from the filtered concentrated solutions in alcohol or in acetic acid, a substance was isolated which was only partially soluble in these solvents.

This can be explained by the probable conversions of the monoamino derivative, which contains active carbonyl groups and an unsubstituted hydrogen atom on the amine nitrogen and is, consequently, capable of polymerization with the formation of polymers which are distinguished by poorer solubility in organic solvents. The tendency of monoaminoquinones toward polymerization was noted rather long ago [6].

EXPERIMENTAL

Disulfanilamidoquinones

2,5-Disulfapyridinobenzoquinone. We dissolved 2.5 g (0.01 mole) of sulfidine by heating it with a reflux condenser in 100 ml of alcohol and added a solution of 2.2 g (0.02 mole) of benzoquinone in 100 ml of hot water to the solution obtained, which was being stirred. The mixture acquired a red color and a light brown precipitate quickly settled out. The mixture was stirred and boiled for 3 hours. The precipitate was filtered off and washed with alcohol. We boiled it in a flask with a reflux condenser in 150 ml of 80% acetic acid to purify it. After cooling, the precipitate was filtered off and repeatedly washed with hot acetic acid. The yield was 2.68 g.

0,1132, 0,1157 g sub.: 0.0897, 0.0893 g $BaSO_4$. Found %: S 10.85, 10.58. $C_{28}H_{22}O_6N_6S_2$. Calculated %: S 10.69.

2,5-Disulfathiazolobenzoquinone. 2.5 g (0.01 mole) of sulfathiazole was dissolved by heating on a water bath with a reflux condenser in 100 ml of alcohol, to which we added 200 ml of water. When all the substance had dissolved, 2.2 g (0.02 mole) of benzoquinone was added to the solution and the heating was continued for 3 hours more while the solution was stirred. The precipitate was filtered off and washed with hot water. It was then treated several times with 80% acetic acid in a flask with a reflux condenser, and dried. The yield was 2.65 g.

0.1281, 0.1227 g sub.: 0.1904, 0,1826 g $BaSO_4$. Found %: S 20.36, 20.38. $C_{24}H_{18}O_6N_6S_4$. Calculated %: S 20.91.

2,5-Disulfapyrimidinobenzoquinone. We dissolved 2.5 g (0.01 mole) of sulfapyrimidine in 100 ml of alcohol in a flask with a reflux condenser. 2.2 g (0.02 mole) of benzoquinone was added to the solution which still contained a small quantity of undissolved sulfapyrimidine and the heating was continued for 5 hours more while the mixture was being stirred. The dark brown precipitate was filtered off, washed with hot water and treated several times with boiling 50% acetic acid in a flask with a reflux condenser and dried. The yield was 2.3 g.

0.1387, 0.1163 g sub.: 0.1077, 0.0922 g $BaSO_4$. Found %: S 10.61, 10.86. $C_{26}H_{20}O_6N_8S_2$. Calculated %: S 10.59.

Monosulfanilamidoquinones

Sulfanilamidobenzoquinone. 43 g (0.4 mole) of the benzoquinone was dissolved in 2 liters of water heated to 60° and poured while being stirred into a flask which contained 3.5 liters of cold water and 0.5 liters of saturated

NaCl solution. When the solution obtained had come to room temperature, a hot solution of 9 g (0.05 mole) of streptocidin in 100 ml of alcohol was poured into it while it was being stirred. A flocculent cherry-red precipitate settled out of the mixture, which had become red. After three days, the precipitate was filtered off, washed with water and dried in air. It was then twice treated, in a flask with a reflux condenser, with boiling alcohol in portions of 200 and 100 ml, and each time the insoluble residue from the filtration was washed with alcohol.

5 g of alcohol-insoluble residue of disulfanilamidoquinone was obtained. The combined alcoholic solution after the repeated filtration was diluted with water, which contained 10% sodium chloride for better coagulation of the precipitate. The precipitate of monosulfanilamidoquinone which was formed was filtered off, washed with water and dried. The yield was 7.6 g. The monosulfanilamidoquinone was again reprecipitated from alcohol for purification.

0.1115, 0.1405 g sub,: 0.0860, 0.1088 g $BaSO_4$. Found %: S 10.58, 10.60. $C_{12}H_{10}O_4N_2S$. Calculated %: S 11.51.

Sulfapyridinoquinone. 5 g (0.02 mole) of sulfidine was dissolved in 100 ml of alcohol by boiling in a flask with a reflux condenser and the hot solution obtained was poured into a flask containing 3 liters of water and 1 liter of a saturated NaCl solution. After stirring, 15 g (0.14 mole) of a solution of benzoquinone in 1 liter of hot water was added to it and the volume of the solution was brought with water to 6 liters. After 3 days the precipitate was filtered off, washed with water and dried. It was then twice treated in a flask with a reflux condenser with boiling 96% acetic acid in 200 and 100 ml portions, filtered off and washed with acetic acid. After drying, 1.5 g of disulfapyrimidinoquinone was obtained.

The combined acetic acid solution was filtered once more and diluted with a large quantity of water. Brown flakes of monosulfapyridinoquinone thereupon precipitated and were filtered off, washed well with water and dried. The yield was 3.4 g. The monosulfapyridinoquinone was again reprecipitated from 96% acetic acid for purification.

0.1197, 0.1204 g sub.: 0.0791, 0.0794 g $BaSO_4$. Found %: S 9.07, 9.80. $C_{17}H_{13}O_4N_3S$. Calculated %: S 9.01.

SUMMARY

The preparation of disulfapyridinoquinone, disulfathiazoloquinone and disulfapyrimidinoquinone, and also of monosulfanilamidoquinone and monosulfapyridinoquinone was described.

In contrast to the disulfanilamidoquinones, the monosulfanilamidoquinones are quite soluble in alcohol and in acetic acid. When such solutions are let stand and particularly when they are heated, the monosulfanilamidoquinones are gradually converted into insoluble substances which are probably polymerization products.

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* See Consultants Bureau Translation, page 539.

** See Consultants Bureau Translation, page 533.

[illegible] alcohol. When the solution [illegible] proportion to 180 ml of alcohol was poured into it while it was being stirred. A [illegible] was salted out of the mixture, which had [illegible]. After some time, the precipitate [illegible] with water and dried in air. It was then [illegible] in portions of 250 and 100 ml, and each time the [illegible]

6 g of alcohol-[illegible] was obtained. The [illegible] that the [illegible] and filtration was diluted with water, which contained [illegible] of the precipitate. The precipitate [illegible] which was formed was filtered off, washed with water and dried. The yield was 7.6 g. The [illegible] was [illegible] from alcohol for purification.

0.1116, 0.1106 g sub.: 0.0882, 0.1008 g BaSO₄. Found %: S 10.86, 10.86. Calculated %: S 11.01.

[illegible]quinone. 5 g (0.05 mole) of [illegible] was dissolved in 250 ml of alcohol by boiling in a flask with a reflux condenser, and the hot solution obtained was poured into a [illegible] containing [illegible] of water and 1 liter of a saturated NaCl solution. After stirring, 10 g [illegible] of a solution of [illegible] in 1 liter of hot water was added to it and the volume of the solution was brought up [illegible]. After [illegible] the precipitate was filtered off, washed with water and dried. It was [illegible] in a flask with a reflux condenser with [illegible] acetic acid [illegible] and 100 ml [illegible]. After [illegible] 1.5 g of [illegible] was obtained.

The concentrated acetic acid solution was filtered when warm and diluted with a large quantity of water; [illegible] precipitated and were filtered off, washed with water and dried. The yield was 3.4 g. The [illegible] was [illegible] for purification.

0.1191, 0.1306 g sub.: [illegible] g BaSO₄. Found %: S [illegible]. Calculated %: S 8.01.

SUMMARY

The preparation of [illegible] and [illegible], and also of [illegible] was described.

[illegible]

LITERATURE CITED

(1) [illegible] and Z. [illegible], J. Gen. Chem. [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

(5) [illegible]

(6) [illegible]

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* See Consultants Bureau Translation, page 698.

** See Consultants Bureau Translation, page [illegible].

INVESTIGATION IN THE FIELD OF QUINONES

IX [1]. REACTION OF METHOXYQUINONES WITH AMINES

I. S. Ioffe and A. F. Sukhina

The influence of the methoxy group on the course of a process was established in the study of the chlorination of methoxyquinones [2]. We decided to study the influence of the methoxy group on the reaction of quinones with amines, and, in particular, with aniline and with certain sulfanilamides.

When an alcoholic solution of aniline and methoxyquinone (I) is heated with an excess of the latter, the solution becomes raspberry colored. Upon cooling the solution, the reaction product crystallizes in the form of dark red needles with a constant m.p. of 160°. Analytical determinations showed that the molecule of the compound being formed contains 1 methoxy group and 1 phenylamino group. The distribution of these groups with respect to each other remained unknown. The following observation assisted in the solution of the problem: on heating an alcoholic solution of the starting materials with excess aniline, the raspberry color which initially appeared quickly disappears and another reaction product precipitates from the solution, which is not soluble in alcohol and, as regards the manner of its formation, is evolved in the form of red crystalline spangles. This substances proved to be identical with the dianilinoquinone (III) which was obtained for the first time as early as 1863 [3] by heating aniline with p-benzoquinone (IV). Dianilinoquinone is formed by heating aniline and the above-described methoxyanilinoquinone with a m.p. of 160°. It follows from this that, in this compound, the methoxy and phenylamino groups are located in the para-position to each other (II).

The substance, to which was ascribed the structure of 2-methoxy-5-anilinoquinone (II), was described in the literature [4] as having the form of brown needles with a m.p. of 189°. However, this substance was not obtained via the reaction of methoxyquinone with aniline, but by a roundabout route from 2-hydroxy-5-anilinoquinonanil, by heating the latter with methyl alcohol and strong sulfuric acid. The use in the concluding stage of strong sulfuric acid which has so energetic an action on quinones, raises doubt as to the degree of purity or as to the correctness of the structure of the substance obtained under these conditions. Our experiments showed that 2-methoxy-5-anilinoquinone has a dark red color and melts sharply at 160°.

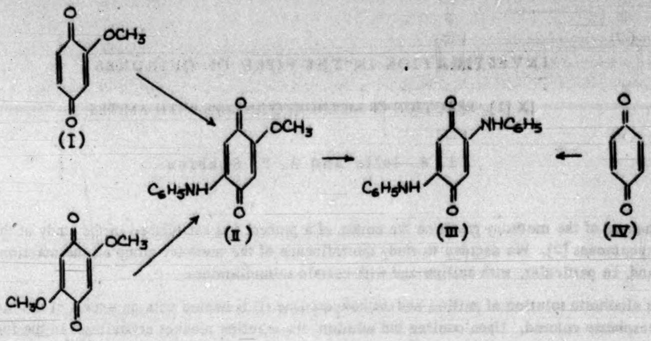
The experiments described above show that, in the reaction of methoxyquinone with amines, the former initially adds one amino radical in the para position to the methoxy group, and then, in the presence of excess amine, the replacement of the methoxy group by another amino radical occurs.

In view of this, we decided to study the reaction between amines and 2,5-dimethoxyquinone (V). It turned out that when 2,5-dimethoxyquinone is heated with aniline in the presence or in the absence of solvents, 2,5-dianilinoquinone is also formed. In contrast to the other substituted quinones, 2,5-dimethoxyquinone reacts with amines only with replacement of the methoxy groups by amine radicals. It also proved possible to carry out this replacement in stages. Upon heating a solution of 2,5-dimethoxyquinone in glacial acetic acid with a small quantity of aniline (1 mole of aniline per 2 moles of dimethoxyquinone), the solution becomes red colored and a dark red precipitate is formed from the solution upon dilution which, after crystallization, was identified as 2-methoxy-5-anilinoquinone.

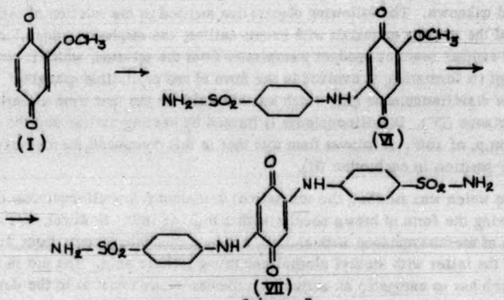
The transformations of methoxyquinone and 2,5-dimethoxyquinone studied by us can be represented by Scheme A.

We obtained analogous results in the reaction of methoxyquinone (I) with sulfanilamide. On heating an alcoholic solution of a mixture of substances with excess quinone, 2-methoxy-5-sulfanilamidoquinone (VI), which crystallizes from glacial acetic acid in the form of reddish-brown prisms with a m.p. of 279-280°, is formed. On heating this substance with sulfanilamide or on heating an alcoholic solution of methoxyquinone and sulfanilamide with an excess of the latter, the fine spangles of disulfanilamidoquinone (VII), previously described by Postovsky and Pushkareva [5] precipitate. (See Scheme B.)

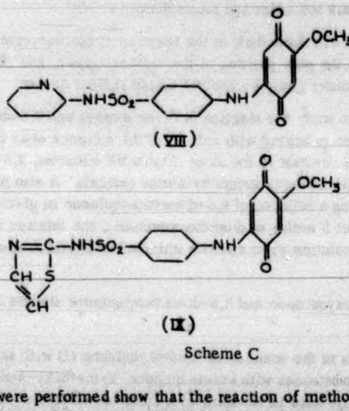
When we carried out this methoxyquinone reaction with sulfapyridine and sulfathiazole, we obtained, respectively, 2-methoxy-5-sulfapyridinoquinone (VIII) and 2-methoxy-5-sulfathiazoloquinone (IX), which melted at 273° and 245°. (See Scheme C.)


OCH3
(I)
OCH3
C6H5NH
(II)
NHC6H5
C6H5NH
(III)
(IV)
OCH3
CH3O
(V)

Scheme A


OCH3
(I)
OCH3
NH2—SO2—
—NH
(VI)
NH—
—SO2—NH2
NH2—SO2—
—NH
(VII)

Scheme B


OCH3
N
—NHSO2—
—NH
(VIII)
OCH3
N=C—NHSO2—
—NH
CH S
CH
(IX)

Scheme C

The experiments which were performed show that the reaction of methoxyquinones with amines proceeds in two directions: with the addition of the amino radical to the unsubstituted carbon atom of the quinone nucleus in one direction; and with replacement of the methoxy group by the amino group in the other. Under the influence of the methoxy group, the amino radical initially, and with greater speed, adds to the unsaturated carbon atom of the quinoid nucleus, necessarily in the para-position to the methoxy group. With excess amine, even under the influence of the available amino group, the methoxy group in the para-position to the latter is replaced by a second amino radical and the reaction is concluded at this point. In the 2,5-dimethoxyquinone, in which both methoxy groups are located in the para-position to each other, replacement of these groups by the amino radicals is still possible and proceeds in stages.

The experimental facts presented in a recently published work [6], are in complete accord with these conclusions; it was shown in this work that on heating either methoxyquinone or 2,5-dimethoxyquinone with excess methylamine, 2,5-di-(methylamino)-quinone is formed. 6-Methoxy-2,5-di-(methylamino)-quinone was not obtained from the 2,6-dimethoxyquinone. These data confirm that the reaction of methoxyquinones with amines proceeds in the two directions indicated above. The authors of the work cited did not analyze both these directions and, consequently, did not establish the laws governing the present reaction.

EXPERIMENTAL

Reaction of Methoxyquinone with Aniline

Preparation of 2-methoxy-5-anilinoquinone. 5 g (2 moles) of methoxyquinone was heated with 75 ml of alcohol until it was completely dissolved. 1.5 g (1 mole) of aniline was added to the boiling solution and it was boiled for 2 hours on a water bath. After cooling, a precipitate in the form of fine dark red needles settled out from the dark red solution.

The precipitate was filtered off, washed with a small quantity of alcohol and dried over calcium chloride. The weight of the precipitate was 3.5 g. After 2-fold crystallization from 50% aqueous alcohol, long dark red needles with a m.p. of 160° were obtained. This substance was moderately soluble in water, and soluble in alcohol, benzene and toluene.

0.1271, 0.1240 g sub.: 0.1316, 0.1285 g AgI (Zeisel). 0.1742, 0.1576 g sub.: 7.88, 7.00 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: OCH_3 13.68, 13.68; N 6.31, 6.22. $C_{13}H_{11}O_3N$. Calculated %: OCH_3 13.54; N 6.57.

Preparation of dianilinoquinone. a) From 2-methoxy-5-anilinoquinone. 1 g of 2-methoxy-5-anilinoquinone was dissolved in 50 ml of boiling acetic acid and 1 g of aniline was added. Precipitation thereupon began. The solution was boiled for 2 hours and was again filtered while hot. The precipitate which settled out in the form of spangles (1.2 g) was not soluble in alcohol or acetic acid and crystallized from nitrobenzene. Shiny dark red flakes, identified as 2,5-dianilinoquinone, were obtained; the melting point was above 300°. The analytical determinations demonstrated the complete absence of methoxy groups.

b) From methoxyquinone. 5 g (1 mole) of methoxyquinone was dissolved in 75 ml of boiling alcohol and 8.5 g of aniline (2.5 moles) was added. After boiling for 2 hours, the precipitate of 2,5-dianilinoquinone was filtered off from the hot solution. Its weight was 6 g.

Reaction of Methoxyquinone with Sulfanilamide

5 g (2 moles) of methoxyquinone was dissolved in 75 ml of boiling alcohol and 2.5 g (1 mole) of sulfanilamide was added to the boiling solution. The solution obtained was boiled for 2 hours and after cooling, the precipitate which settled out was filtered off. Its weight was 3 g. After 3-fold crystallization from glacial acetic acid, fine reddish-brown prisms with a m.p. of 279-280° were obtained. The substance was weakly soluble in water and was soluble in alcohol and glacial acetic acid. Upon boiling in an acetic acid solution with excess sulfanilamide, it was converted into the disulfanilamidoquinone.

0.1726, 0.1537 g sub.: 0.1320, 0.1190 g AgI (Zeisel). 0.1628, 0.1954 g sub.: 12.15, 14.96 ml 0.1 N H_2SO_4 (Kjeldahl). Found %: OCH_3 10.11, 9.58; N 10.44, 10.70. $C_{13}H_{12}O_5N_2S$. Calculated %: OCH_3 10.07, N 9.1.

Reaction of Methoxyquinone with Sulfidine

5 g (2 moles) of methoxyquinone was dissolved in 75 ml of boiling alcohol and 4 g (1 mole) of sulfidine was added to the boiling solution. The solution obtained was boiled with continuous stirring for 2 hours and after cooling, the light red precipitate which settled out was filtered off. Its weight was 3.5 g.

After 2-fold crystallization from 80% acetic acid, shiny light red petals with a m.p. of 273° (with decomposition) were obtained. The substance was insoluble in water and alcohol. It was soluble in a ratio of 1:250 in 80% acetic acid.

Sulfur determination, by Messinger's method:

0.1543, 0.1372 g sub.: 0.0878, 0.0805 g $BaSO_4$. Found %: S 7.98, 7.75. $C_{19}H_{15}O_5N_3S$. Calculated %: S 8.06.

Reaction of Methoxyquinone with Sulfathiazole

5 g (2 moles) of methoxyquinone were dissolved in 75 ml of boiling alcohol and 4.5 g (1 mole) of sulfathiazole was added to the hot solution. The solution obtained was boiled for 2 hours and after cooling, the precipitate which settled out was filtered off. Its weight was 3 g. After 2-fold crystallization from 60% acetic acid, a finely crystalline Bordeaux red precipitate with a decomposition temperature of 245-247° was obtained. The substance was insoluble in water, benzene and ether and was weakly soluble in alcohol, and soluble in glacial and dilute acetic acid.

Sulfur determination, by Messinger's method:

0.1844, 0.1670 g sub.: 0.2214, 0.1996 g $BaSO_4$. Found %: S 16.33, 16.27. $C_{16}H_{13}O_5N_3S_2$. Calculated %: S 16.36.

Reaction of 2,5-Dimethoxyquinone with Aniline

Preparation of dianilinoquinone. 1 g of 2,5-dimethoxyquinone was dissolved in 75 ml of boiling acetic acid and 1 g of aniline was added. Under these conditions the solution was initially red colored, but spangles of a substance which was insoluble in acetic acid quickly began to precipitate. The mixture was boiled for 2 hours and the precipitate was filtered off from the hot solution. Its weight was 1 g. The reaction product did not contain methoxy groups. After crystallization from nitrobenzene the 2,5-dianilinoquinone was obtained in the form of shiny brown flakes with a melting point above 300°.

Preparation of 2-methoxy-5-anilinoquinone. 1 g of 2,5-dimethoxyquinone (2 moles) was dissolved in 75 ml of boiling acetic acid, 0.3 g of aniline (1 mole) was added and the mixture was boiled for 2 hours. The red solution obtained was concentrated to 10 ml and after cooling was diluted with 90 ml of water; the precipitate which settled out was filtered off. Its weight was 0.8 g. After 3-fold crystallization from 50% aqueous alcohol, dark red needles of a substance with a m.p. of 160° were obtained, which were identified as 2-methoxy-5-anilinoquinone.

SUMMARY

The corresponding 2-methoxy-5-aminoquinones were obtained by the reaction of methoxyquinone with aniline, sulfanilamide, sulfapyridine and sulfathiazole. On treating 2-methoxy-5-phenylaminoquinone with excess aniline, as well as during the direct reaction of methoxyquinone with excess aniline, dianilidoquinone is formed. The same product is obtained by heating aniline and 2,5-dimethoxyquinone together. Analogous results are obtained by heating methoxyquinone with excess sulfanilamide.

The reaction of methoxyquinones with amines proceeds in two directions – in one, with the addition of an amino radical to the unsubstituted carbon atom of the quinoid nucleus, and in the other, with replacement of the methoxy group by an amino group.

Under the influence of the methoxy group, the amino radical adds to the unsubstituted carbon atom, if there is any, at a great rate and in the para-position to the amino group. Replacement of the methoxy group by one more amino radical in the presence of excess aniline still proceeds at lower rate and is necessarily in the para-position to the amino group already present. 2,5-Dimethoxyquinone reacts only with replacement of the methoxy groups and this replacement proceeds in stages.

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* See Consultants Bureau Translation, page 715.

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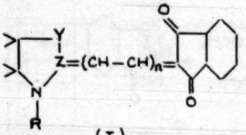
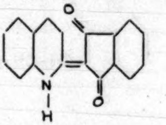
THE COLOR OF CERTAIN MEROCYANIN DYES WHICH ARE DERIVATIVES OF INDANDIONE-1,3

V. G. Zhiryakov and I. I. Levkoev

Mercoyanines, which are derivatives of indandione-1,3 (I) containing an external polymethine chain, have been studied very little [1-4] up to now, although the simplest dyes of this group, which contain the quinoline residue, are known under the name of "quinophthalones"(II) and have been subjected to detailed investigations [5-8]:



(I)



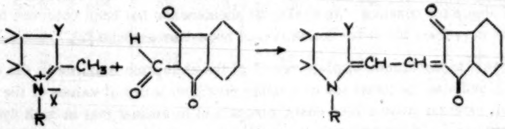
(II)

Ordinary quinophthalones, which contain hydrogen on the nitrogen atom of the heterocyclic radical – the sulfo acids of which are used as yellow acid dyes – have been prepared by the reaction of phthalic anhydride with quinaldine [5]. However, the N-alkyl derivatives of the quinophthalones [8] are also known.

The merocyanine dyes, which contain the indandione-1,3-radical, are of considerable interest in the study of the relation between color and structure, since due to the presence of two carbonyl groups in them, very considerable electron displacement from the nitrogen atom of the heterocyclic radical is probable, and this has actually been confirmed for a few dimethine dyes of this group [2, 3].

In this connection, we synthesized a number of di-, tetra- and hexamethin-merocyanines – derivatives of indandione-1,3 with the radicals 3,3-dimethylindolenine, benzthiazole and 4,5-diphenylthiazole which have respectively low, average and high basicity; the optical properties of these dyes were studied.

Dimethinmerocyanines with the 3,3-dimethylindolenine, benzthiazole and 4,5-diphenylthiazole radicals were synthesized via the condensation of 2-formyl-3-hydroxyindenone-1 with the quaternary salts of the corresponding 2-methyl-substituted heterocyclic bases by heating with anhydrous ethyl alcohol in the presence of triethylamine:

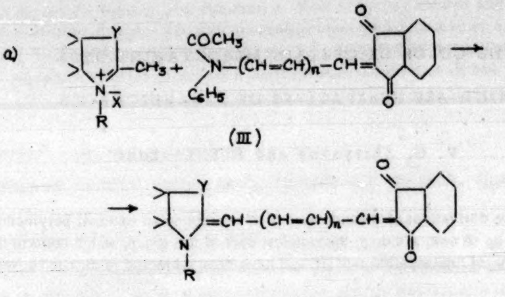


The tetra- and hexamethinmerocyanines were prepared analogously, starting with 2,β-acetanilinoallyliden- and pentadienylidenindandione-1,3 (III) (see a).

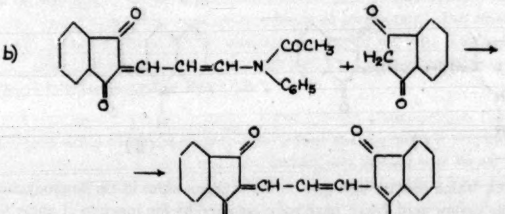
With the object of calculating "hypsochromic displacement" of the absorption maxima of the merocyanines obtained, oxanine dyes were synthesized – derivatives of indandione-1,3 with 3 and 5 methine groups in the external polymethine chain.

Trimethinoxanine (IV) was prepared by the reaction of 2-β-acetanylinoallylidenindandione-1,3 with indandione-1,3 by heating with anhydrous ethyl alcohol in the presence of triethylamine (see b).

Pentamethinoxanine was successfully prepared by the direct condensation of indandione-1,3 with the hydrochloride of the dianil of glutaconic aldehyde under analogous conditions.



(III)



(IV)

The majority of the dyes obtained were chromatographed on active aluminum oxide for purification.

In Table 1 are presented the absorption maxima of the merocyanines obtained, the "hypsochromic displacement" of their absorption maxima in comparison with that calculated for the corresponding symmetric oxanines and cyanines, and also the bathochromic displacement of the absorption maxima caused by lengthening the external polymethine chain by one vinylene group.

The absorption maxima of the salts of the mono-, tri- and pentamethinoxanines — derivatives of indandione-1,3 — lie at 459, 551 and 650 mμ, respectively.

In considering the data presented in Table 1, one's attention is, first of all, attracted to the anomalously small magnitudes of the "hypsochromic displacements" of the absorption maxima of all the di-, tetra- and hexamethinmerocyanines, which are derivatives of indandione-1,3. In addition, the dyes which are derivatives of indandione-1,3, upon elongation of the polymethine chain, in a number of cases form not a congruent, but even a rather divergent series of absorption maxima. An analogous phenomenon has been observed previously to a lesser extent only for certain merocyanines which are derivatives of phenylisoxazolone [2].

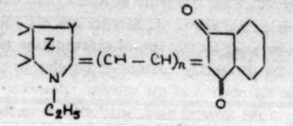
The very insignificant "hypsochromic displacement" of the absorption maxima in the dyes which are derivatives of indandione-1,3, and also the formation of a rather divergent series of values of the absorption maxima formed on elongating their external polymethine chain, compels us to assume that in such dyes the electron displacement from the nitrogen atom of the heterocyclic residue is very great. As a result of such displacements, in the majority of such dyes, evidently, a comparatively regular distribution of the electron density in the polymethine chromophore is brought about and is chiefly responsible for their deep color.

The position of the absorption maxima of the merocyanine dyes, which are derivatives of indandione-1,3, in solvents of varying polarities was measured with the object of confirming these assumptions. Such measurements, to elucidate the character of the distribution of the electron density in the molecules of the merocyanine dyes, are usually carried out in several different solvents [9, 10]. As a rule, methyl or ethyl alcohol, benzene, chloroform, etc. are used for this purpose.

This method has a substantial disadvantage that consists in the fact that it is impossible to use it to regularly proceed from a less polar to a more polar solvent; this is of great importance in this kind of investigations.

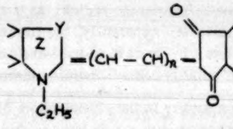
A large number of other factors besides the dielectric constant of the solvent influence the structure and, consequently, the position of the absorption maximum of the merocyanine (for example, the possibility of the

TABLE 1



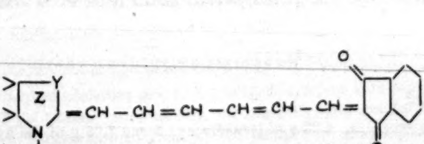
Z	n	Absorption maximum in ethyl alcohol (in mμ)		Vinylenic displacement of the absorption maximum (in mμ)	Hypsochromic displacement (in mμ)
		of the corresponding cyanine	observed for the merocyanine		
3,3-Dimethylindolenine	1	546	495	–	7.5
	2	634	588	93	4.5
	3	746	684	96	14.0
Benzthiazole.	1 [1]	558	506	–	2.5
	2	654	596	92	4.5
	3	763	706	108	0.5
4,5-Diphenylthiazole . .	1	588	520	–	3.5
	2	683	611	91	6.0
	3	–	722	111	–

TABLE 2



Z	n	Absorption maximum (in mμ)							
		percent content by weight of n-decyl alcohol in the mixture							in ethyl alcohol
		0	20	40	60	80	90	100	
3,3-Dimethylindolenine	1	493	–	–	495	495	–	495	495
	2	584	584	586	588	588	586	586	588
Benzthiazole	1	502	–	505	507	–	–	509	506
	2	594	597	600	601	603	603	602	598
4,5-Diphenylthiazole . .	1	516	–	–	520	522	–	525	520
	2	605	608	–	615	617	–	620	611

TABLE 3



Z	Absorption maximum (mμ)				
	percent content by weight of n-decyl alcohol in the mixture				in ethyl alcohol
	0	40	60	100	
3,3-Dimethylindolenine	686	684	683	675	684
Benzthiazole.	706	706	706	705	706
4,5-Diphenylthiazole . .	714	724	732	738	722

formation of hydrogen bonds, the dipole moment and others); these depend on the chemical nature of the solvents used and, consequently, the use of solvents which are markedly different from each other in their nature, is also a rather considerable defect in the method described above. L. Brooker and his coworkers in their latest work [2-4] have eliminated the first of these defiects by using for this sort of investigation mixtures of pyridine and water, which vary considerably in their polarity; the percentage content of pyridine in the mixtures is varied gradually which made it possible to regularly change the polarity of the solvent. However, the second defect, to wit, the marked difference in the chemical nature of the solvents used, still remains in this work, which does not make is possible to consider the results obtained by these authors as entirely reliable.*

We selected methyl and n-decyl alcohols and their mixtures to obtain more precise results in the investigation of the structure of the dyes which are derivatives of indandione-1,3 in solvents of varying polarity. These alcohols were used as solvents because they are representatives of the same homologous series, have approximately equal dipole moments (1.69 and 1.63), but markedly differ in the magnitude of their dielectric constants.

The results of these measurements, for di-, tetra- and hexamethinmerocyanine dyes which are derivatives of indandione-1,3, are presented in Tables 2 and 3.

It is evident from consideration of Table 2 that the color of di- and tetramethinmerocyanines with 3,3-dimethylindolenine radicals remains practically unchanged with change in the polarity of the solvent. It can be supposed that there is a comparatively regular distribution of the electron density along the polymethine chain in the molecules of these dyes or that their structure is insignificantly displaced toward that of an internal-ionic structure.

Di- and tetramethinmerocyanines with benzthiazole and 4,5-diphenylthiazole radicals have an appreciably deeper color (7-15 mμ) with diminishing polarity of the solvent. Evidently, the structure of their molecules in methanol is displaced toward that of the internal-ionic structure, and the irregularity in the distribution of the electron density along the chain is intensified as the basicity of the heterocyclic radical is increased.

Hexamethinmerocyanine with a 3,3-dimethylindolenine radical, as is evident from the data of Table 3, increases its color as one proceeds to less polar solvents. Apparently, the structure of a molecule of this dye even in methanol is displaced toward a covalent structure. In the case of the hexamethine dye with a benzthiazole radical, the color remains practically unchanged as the polarity of the solvent is diminished.

Evidently, the distribution of the electron density in the chromophore of this dye is comparatively regular. The absorption maximum of hexamethinmerocyanine with a 4,5-diphenylthiazole radical is displaced into the short wave portion of the spectrum with increasing polarity of the solvent. The structure of this dye evidently remains displaced toward that of the internal-ionic in all the solvents investigated.

The experiments which were carried out show that for the dyes which are derivatives of indandione-1,3, the relationship between their color and structure is basically the same as for merocyanines with radicals of other ketomethylenic compounds. However, the structure of the majority of them, particularly those with a short polymethine chain, is more correctly depicted by the internal-ionic formula. With lengthening of the chain of these merocyanines, the structure of their molecules is gradually displaced toward a covalent structure, the more rapidly, the less basic the nitrogenous heterocyclic radical which is included in the dye molecule. In general, however, as regards dyes which are similar to merocyanines, the derivatives of the majority of other ketomethylenic compounds are characterized by considerable stability relative to the regular distribution of the electron density in the polymethine chromophore and lowering of the polarity. The latter apparently gradually increases with lengthening of the chain of such merocyanines.

EXPERIMENTAL

1. Intermediate Products

2-(Anilinoallyliden)-indandione-1,3. 4.38 g of indandione-1,3 and 7.75 g of the hydrochloride of the dianil of malonic aldehyde were dissolved in 60.0 ml of anhydrous ethyl alcohol in a flask with a reflux condenser, and 3.0 g of triethylamine was added to the solution. The mixture was heated for 30 minutes on a boiling water bath. After cooling, the precipitate which settled out was filtered off, washed with ethyl alcohol and dried. The yield was 5.7 g (69.2%); m.p. 239-240°. After crystallization from ethyl alcohol, 5.1 g of a substance in the form of dark red needles with a m.p. of 242-243° was obtained. There was an absorption maximum at 530 mμ (in ethyl alcohol).

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* It is necessary to mention that L. Brooker and his coworkers tried to explain a portion of his experimental data from the point of view of the basically faulty "theory of resonance".

Found %: N 5.15. $C_{18}H_{13}O_2N$. Calculated %: N 5.09.

2-(Acetanilinoallyliden)-indandione-1,3 was prepared by acetylating the preceding compound (5.1 g) with acetic anhydride (30.0 ml) in the presence of triethylamine (2.1 g) while the solution was being boiled (25 minutes). The precipitate which settled out on cooling was filtered off, washed with water and ethyl alcohol, and dried. The yield was 76.6%. It consisted of dark yellow needles with a m.p. of 244-245° (from ethyl alcohol).

Found %: N 4.51. $C_{20}H_{15}O_3N$. Calculated %: N 4.42.

2-(Anilinopentadienyliden)-indandione-1,3. 1.46 g of indandione-1,3 and 2.84 g of the chloride of the dianil of glutaconic aldehyde were dissolved by heating in 25.0 ml of anhydrous ethyl alcohol, and 1.01 g of triethylamine was added to the solution; an intense dark blue color thereupon appeared and a precipitate began to settle out. The mixture was heated for 20 minutes on a boiling water bath. After cooling, the precipitate was filtered off, carefully washed with ethyl alcohol and acetone until the filtrate had a pure violet color, and dried. The yield was 1.75 g (58.2%), m.p. 189-190°. After crystallization from benzene, 1.38 g of a substance in the form of dark violet needles with a m.p. of 193-194° was obtained. There was an absorption maximum at 560 mμ (in ethyl alcohol).

Found %: N 4.80. $C_{20}H_{15}O_2N$. Calculated %: N 4.65.

2-(Acetanilinopentadienyliden)-indandione-1,3 was synthesized by acetylating the preceding compound (1.75 g) with acetic anhydride (5.0 ml) in the presence of triethylamine (0.58 g) while the solution was being boiled (10 minutes). The precipitate which settled out after cooling was filtered off, washed with water and ethyl alcohol and dried. The yield was 78.8%. It consisted of fine light brown needles with a m.p. of 237-238° (from benzene).

Found %: N 4.25. $C_{22}H_{17}O_3N$. Calculated %: N 4.08.

2. Dyes

2-(1'-Ethyl-3',3'-dimethylindolinyliden-2'-ethyliden)-indandione-1,3

0.16 g of 2,3,3-trimethylindolenine and 0.16 g of diethyl sulfate were heated in a flask with a reflux condenser on a water bath at 80° for 60 minutes. After cooling, the quaternary salt was dissolved by heating it in 4.0 ml of anhydrous ethyl alcohol, and 0.17 g of 2-formyl-3-hydroxyindenone-1 and 0.1 g of triethylamine were introduced into the solution. The liquid was heated on a boiling water bath for 15 minutes.

After cooling, the precipitated dye was filtered off, washed with ethyl alcohol and dried. The yield was 0.14 g (40.8%), m.p. 201-203°.

Found %: N 4.12. $C_{23}H_{11}O_2N$. Calculated %: N 4.08.

2-(3'-Ethyl-4',5'-diphenylthiazolinyliden-2'-ethyliden)-indandione-1,3

0.41 g of the iodoethylate of 2-methyl-4,5-diphenylthiazole and 0.17 g of 2-formyl-3-hydroxyindenone-1 were dissolved in 4.0 ml of anhydrous ethanol in a flask with a reflux condenser. 0.11 g of triethylamine was introduced into the solution and a dark red color appeared at once. The liquid was heated on a boiling water bath for 15 minutes. After cooling, the precipitated dye was filtered off, washed with ethyl alcohol and dried. The yield was 0.20 g (45.9%), m.p. 279-280°. After crystallization from ethyl alcohol it consisted of reddish-orange needles with a m.p. of 288-289°.

Found %: N 3.20. $C_{28}H_{21}O_2NS$. Calculated %: N 3.21.

2-(1'-Ethyl-3',3'-dimethylindolinyliden-2'-butenyliden)-indandione-1,3

0.33 g of 2,3,3-trimethylindolenine and 0.32 g of diethyl sulfate were heated in a flask with a reflux condenser on a water bath at 80° for 1 hour. After cooling, the quaternary salt was dissolved by heating in 11.0 ml of n-butyl alcohol and 0.64 g of 2-(acetanilinoallyliden)–indandione-1,3 and 0.25 g of triethylamine were introduced into the solution. The liquid was boiled for 1 hour. After cooling, the dye which was formed was filtered off, washed with ethyl alcohol and dried.

The yield was 0.36 g (48.6%), m.p. 237-238°. After chromatographic purification of a chloroform solution of the dye on active aluminum oxide and crystallization from ethyl alcohol, it consisted of coarse violet prisms with a metallic sheen and a m.p. of 249-250°.

Found %: N 3.91. $C_{25}H_{23}O_2N$. Calculated %: N 3.79.

2-(3'-Ethylbenzthiazolinyliden-2'-butenyliden)-indandione-1,3

0.35 g of the ethyl-p-toluenesulfonate of 2-methylbenzthiazole and 0.32 g of 2-(acetanilinoallyliden)-indandione-1,3 were heated in a flask with a reflux condenser with 13.0 ml of anhydrous ethyl alcohol (incomplete solution). 0.11 g of triethylamine was added to the mixture and the liquid was heated on a boiling water bath for 30 minutes. After cooling, the dye which was formed was filtered off, washed with ethyl alcohol and dried. The yield was 0.20 g (55.5%), and the m.p. 238-240°. After two-fold chromatographic purification of a solution of the dye in chloroform on active aluminum oxide and crystallization from benzene, the dye consisted of green needles with a m.p. of 278-279°.

Found %: N 3.93. $C_{22}H_{17}O_2NS$. Calculated %: N 3.89.

2-(3'-Ethyl-4',5'-diphenylthiazolinyliden-2'-butenyliden)-indandione-1,3

0.62 g of the iodoethylate of 2-methyl-4,5-diphenylthiazole and 0.48 g of 2-(acetanilinoallyliden)-indandione-1,3 were dissolved by heating in 11.0 ml of n-butyl alcohol in a flask with a reflux condenser, and 0.17 g of triethylamine was introduced into the solution. The dark blue liquid was boiled for 30 minutes. A precipitate of the dye was formed shortly after the beginning of the heating. After cooling, the dye was filtered off, washed with ethyl alcohol and dried. The yield was 0.66 g (95.5%), m.p. 258-259°. After chromatographic purification of a chloroform solution of the dye on active aluminum oxide and crystallization from ethyl alcohol, it consisted of fine green prisms with a m.p. of 274-275°.

Found %: N 2.80. $C_{30}H_{23}O_2NS$. Calculated %: N 3.03.

2-(1'-Ethyl-3',3'-dimethylindolinyliden-2'-hexadienyliden)-indandione-1,3

0.65 g of the diethyl sulfate of 2,3,3-trimethylindolenine, obtained by the usual method, was dissolved in 5.0 ml of anhydrous ethyl alcohol in a flask with a reflux condenser by heating; the solution was cooled to 50° and 0.35 g of 2-(acetanilinopentadienyliden)-indandione-1,3 and 0.11 g of triethylamine were added to it. The brownish-yellow mixture was heated at 50° (in a mass) for 5 minutes and left for 24 hours at room temperature. The unreacted 2-(acetanilinopentadienyliden)-indandione-1,3 was then filtered off (weight: 0.22 g), the filtrate was concentrated in a vacuum, the residue dissolved in chloroform, and the solution chromatographed three times on active aluminum oxide; a fraction was collected under these conditions which had a pure blue color. After driving off the chloroform in a vacuum and crystallizing the residue from ethyl alcohol, 0.03 g of the dye was obtained in the form of fine dark brown prisms with a m.p. of 146-147°.

Found %: C 82.10; H 6.40. $C_{27}H_{25}O_2N$. Calculated %: C 81.98; H 6.37.

2-(3'-Ethylbenzthiazolinyliden-2'-hexadienyliden)-indandione-1,3

0.35 g of the ethyl-p-toluenesulfonate of 2-methylbenzthiazole and 0.35 g of 2-(acetanilinopentadienyliden)-indandione-1,3 were dissolved in 10.0 ml of n-butyl alcohol in a flask with a reflux condenser which was heated, and 0.11 g of triethylamine was introduced into the solution; an intense dark blue color at once appeared and the dye precipitated. The mixture was boiled for 15 minutes. After cooling, the precipitate of the dye which was formed was filtered off, carefully washed with cold and hot ethyl alcohol and dried. The yield was 0.15 g (41.7%), m.p. 205-206°. After two-fold crystallization from ethyl alcohol it consisted of fine green prisms with a golden tinge which melted at 207-208°.

Found %: N 3.46. $C_{24}H_{19}O_2NS$. Calculated %: N 3.63.

2-(3'-Ethyl-4',5'-diphenylthiazolinyliden-2'-hexadienyliden)-indandione-1,3

0.41 g of the iodoethylate of 2-methyl-4,5-diphenylthiazole and 0.35 g of 2-(acetanilinopentadienyliden)-indandione-1,3 were dissolved in 10.0 ml of n-butyl alcohol in a flask with a reflux condenser which was heated, and 0.11 g of triethylamine was added to the solution.

The greenish-blue mixture was boiled for 20 minutes. After cooling, the dye which separated was filtered off, washed with ethyl alcohol and dried. The yield was 0.25 g (51.0%), m.p. 184-186°. After chromatographic purification of a chloroform solution of the dye on active aluminum oxide and crystallization from ethyl alcohol, it consisted of fine dark green prisms with a golden tinge, which melted at 200-201°.

Found %: N 2.76. $C_{32}H_{25}O_2NS$. Calculated %: N 2.87.

Triethylamine Salt of 2-[3'-Hydroxy-1'-ketoindenyl(1',2')-2-allyliden]-indandione-1,3

0.64 g of 2-(acetanilinoallyliden)-indandione-1,3 and 0.29 g of indandione-1,3 were heated in a flask with a reflux condenser with 8.0 ml of anhydrous ethyl alcohol (incomplete solution). 0.30 g of triethylamine was added to the mixture; an intense violet color at once appeared. The mixture was heated on a boiling water bath for 40 minutes. After cooling, the alcohol was driven off in a vacuum, the residue (a dark violet oil) was dissolved in chloroform, and the solution was chromatographed on active aluminum oxide; a fraction with a pure violet color was collected under these conditions. After driving off the chloroform in a vacuum and crystallizing the residue from 50% ethyl alcohol, 0.12 g of the triethylamine salt of the dye was obtained in the form of fine, dark brown needles with a m.p. above 300°.

Found %: C 75.46; H 6.32: $C_{27}H_{27}O_4N$. Calculated %: C 75.48; H 6.34.

Triethylamine Salt of 2-[3'-Hydroxy-1'-ketoindenyl(1',2')-2''-pentadienyliden]-indandione-1,3

1.46 g of indandione-1,3 and 1.42 g of the hydrochloride of the dianil of glutaconic aldehyde were dissolved in 20.0 ml of anhydrous ethyl alcohol in a flask with a reflux condenser which was heated, and 1.50 g of triethylamine was introduced into the solution. The dark blue liquid was heated on a boiling water bath for 30 minutes. After cooling, the precipitate of 2-(anilinopentadienyliden)-indandione-1,3 formed was filtered off and washed with 3.0 ml of anhydrous ethyl alcohol (the weight of the precipitate was 0.80 g, the m.p. 232-236° and a mixed sample with the pure substance displayed no melting point depression). The filtrate was combined with the wash alcohol and concentrated in a vacuum to a volume of 3.0 ml; an abundant precipitate of the triethylamine salt of the dye thereupon settled out and was filtered off, washed with alcohol and dried in a vacuum over caustic alkali. The yield was 0.20 g (8.7%), the m.p., 148-150°. After crystallization from ethyl alcohol it consisted of dark green prisms with a m.p. of 149-150°.

Found %: C 76.51; H 6.45
$C_{29}H_{29}O_4N$. Calculated %: C 76.44; H 6.42

The absorption spectra of the dyes were measured in a $1 \cdot 10^{-4}$ molar solution with a König-Martens spectrophotometer and in a few cases, with a "UM-2" monochomator.

SUMMARY

1. The synthesis of several di-, tetra- and hexamethinmerocyanines which are derivatives of indandione-1,3, and also of the corresponding tri- and pentamethinoxanines was carried out. The absorption spectra of these merocyanines was investigated in mixtures of solvents which were close in their properties but had varying polarity.

2. It was shown that the majority of the merocyanines which are derivatives of indandione-1,3 are characterized by a comparatively regular distribution of the electron density in the polymethine chromophore and by reduced polarizability.

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INVESTIGATION OF FURAN COMPOUNDS

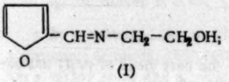
VI. FURAN AND TETRAHYDROFURAN AMINO ALCOHOLS FROM FURFURAL AND β-(α-FURYL)-ACROLEIN

A. A. Ponomarev, V. Pletneva, V. Sedavkina and L. Barskaya

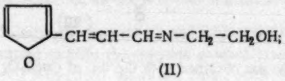
The condensation of furfural with primary aliphatic amines, as is well-known, leads to the formation of the corresponding azomethines.

Very little is known of the reaction of furfural and its vinyl analogs with amino alcohols. In particular, Senkus [1] described a product, prepared from furfural and β-aminoisobutanol, which, in the opinion of the author, was the oxazolidine derivative; upon hydrogenation of the latter, the corresponding furfurylaminoalkanol was formed.

As our experiments have shown, furfural and β-(α-furyl)-acrolein react with monoethanol amine in a mole-for-mole ratio without catalyst, to form the corresponding derivatives in excellent yields. The latter can have the structure of azomethines (I and II) or of their isomeric oxazolidine compounds (III and IV), the formation of which is possible as a result of intramolecular cyclization:



(I)



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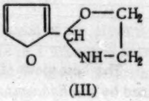

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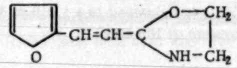
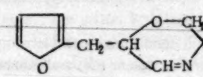


(IV)

In the case of furylacrolein, a third formula with a morpholine ring is also possible:



(V)

The sensitivity of these substances to acidic reagents, oxidizing agents etc., complicates the elucidation of their structure by the usual chemical methods. This applies also to the derivatives of other aldehydes and monoalkanol amines; this can be explained by the fact that the oxazolidine structure ascribed to many of them is, properly speaking, unfounded [2, 3, 4]. In this connection it should be indicated that the study of the infra-red spectra of a number of analogous derivatives of aromatic aldehydes and monoethanol amines gives us a basis for assuming that their structure is azomethinic, but not cyclic (oxazolidinic) [5].

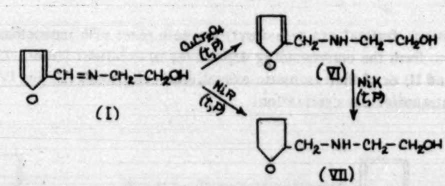
The molecular refraction of the substances obtained by us makes it clear that they have the azomethine structures (I) and (II). Actually, the experimentally found molecular refraction of the first product is 38.82, while that calculated for formula (I) is equal to 37.24 (EMR_D 1.58), and for III, 36.08 (EMR_D 2.74). While the presence of an excited state is a consequence of the structure of the azomethine (the presence of a conjugated exocyclic double bond in the ring), such a considerably excited state can not be explained for the oxazolidine derivative (III) by any structural peculiarities.

In the same way, the observed value of MR_D for the second product amounted to 51.79; that calculated for formula (II) (azomethine), 46.00 (EMR_D 5.78), and for formula (IV), 44.39 (EMR_D 7.40), and for formula (V), 44.85 (EMR_D 6.94). It is evident that in this case, if the structure of the substance was in accord with formula (IV) on (V), the observed experimental MR_D would have had to have been considerably less than occurs, in accord with the considerations already stated in connection with the first product.

In this connection it is impossible not to note that the experimental EMR$_D$ found by us for the products (I) and (II) is in accord in absolute magnitude with the EMR$_D$ of other furan derivatives which have, respectively, one or two double bonds in conjugation with the ring. Thus, for example, the EMR$_D$ of furfural is 1.61, of furylethylene, 1.63 [6], etc.; the EMR$_D$ of furylacrolein is 5.70 [7], of β-(5-methyl-2-furyl)-acrolein is 5.62 [8], of furylbutenone 5.52 [6], etc..

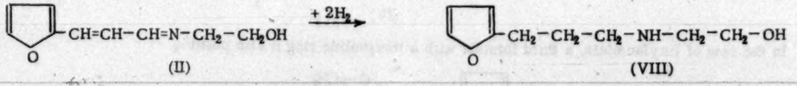
This agreement in the magnitudes of the EMR$_D$ is also a well-known confirmation of the azomethinic nature of the indicated products. In addition, it is evidence of the fact that the double bonds of the $>C=C<$, $>C=O$ and $>C=N-$ type in conjugation with carbon-carbon double bonds of the furan ring exert an almost identical exciting influence.

The experiments involving the hydrogenation of the azomethines were performed in the presence of various catalysts. It was established that the end products of the hydrogenation of furfurylidenaminoethanol (I), depending on the catalyst and the conditions, are either furfurylamino ethanol (VI) or tetrahydrofurfurylaminoethanol (VII), which is illustrated by the following scheme:

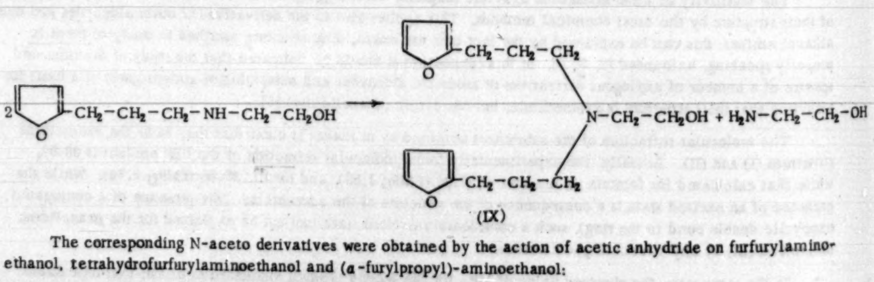


The best yield of (VI) (70-72%) was obtained with the use of $CuCr_2O_4$ while the best yield of (VII) was obtained by the hydrogenation of (VI) with nickel on kieselguhr (NiK) (73%).

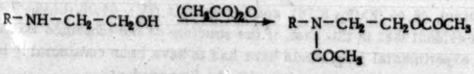
(α-Furylpropyl)-amino ethanol (VIII) was obtained in a yield of 41.5% by the hydrogenation of (II) with Raney nickel (NiR) at 140-160° and a pressure of 100 atm.



When (II) was hydrogenated under other conditions, with the same catalyst (170°, 125 atm), (α-furylpropyl)-amino ethanol (VIII), bis-(α-furylpropyl)-aminoethanol (IX) and monoethanolamine were isolated from the reaction mixture. It can, consequently, be assumed that the process proceeds initially to the formation of (VIII) and then is complicated by a disproportionation reaction of (VIII) into (IX) and monoethanolamine:



The corresponding N-aceto derivatives were obtained by the action of acetic anhydride on furfurylaminoethanol, tetrahydrofurfurylaminoethanol and (α-furylpropyl)-aminoethanol:



$$R-NH-CH_2-CH_2OH \xrightarrow{(CH_3CO)_2O} R-\underset{\displaystyle COCH_3}{\underset{|}{N}}-CH_2-CH_2OCOCH_3$$

Attempts to obtain an azomethine in the pure form from furfurylidenacetone and monoethanolamine were not successful in view of the considerable resinification (particularly on distillation) of the reaction products.

EXPERIMENTAL

The hydrogenation was conducted in steel rotating autoclaves, 0.5 and 0.15 liter in capacity. The temperature was held within the assigned limits by an electronic regulating millivoltmeter. The preparation of the catalysts was as follows: Raney nickel (NiR) was prepared by leaching Ni–Al alloy [9]; copper chromite catalyst ($CuCr_2O_4$) was prepared by the usual method [10]; platinum catalyst was prepared by Adam's method [11]. The nickel on kieselguhr (NiK) was industrial catalyst of Soviet production, which was preliminarily ground and reduced in a stream of hydrogen at 200°.

N-Furfurylidenaminoethanol

In a typical experiment, 27 g of furfural was placed in a three-necked flask, 0.5 liter in capacity, equipped with a mechanical stirrer with an oil seal and a dropping funnel, and then 17.7 g of monoethanolamine was added from the dropping funnel to the flask while the contents of the latter were being stirred over a period of 2 hours. The color of the reaction mixture changed during the experiment from straw-yellow to cherry-brown and the mixture thickened. After the addition of all the monoethanolamine, the contents of the flask were heated for half an hour on a water bath at 60-70° and then were vacuum distilled in a stream of nitrogen. The furfurylidenaminoethanol distilled at 136° (8 mm) and the weight was 27.5 g (70.3%).

d_4^{20} 1.1524; n_D^{20} 1.5561; MR_D 38.82; calculated 37.24.

0.1342 g sub.: 0.2954 g CO_2; 0.0830 g H_2O. 0.1737 g sub.: 15.6 ml N_2 (23.4°, 748 mm). 0.1778 g sub.: 16 ml N_2 (25°, 768 mm). 0.0726 g sub.: 13.6 ml CH_4 (22°, 767 mm). Found %: C 60.07; H 6.92; N 10.34, 10.19; active H 0.76. $C_7H_9O_2N$. Calculated %: C 60.42; H 6.52; N 10.07; active H 0.72.

By conducting the reaction in a nitrogen atmosphere and subsequent vacuum distillation of the product in a stream of nitrogen, the yield was raised to 82%; the reaction product, when not distilled in a stream of nitrogen, has a darker color and a lower index of refraction. However, pure azomethine, which has the above indicated constants, is obtained by repeated vacuum distillation even in this case.

Furfurylidenaminoethanol consisted of a straw-yellow liquid which quickly thickened and darkened in air, and had the characteristic amine odor. It was quite soluble in water, alcohol and ether. The b.p. was 114° (1.5 mm), 123-124° (4 mm).*

Furfurylaminoethanol

110 g of freshly distilled furfurylidenaminoethanol, 140 ml of dioxan and 7 g of copper-chromite catalyst was placed in an 0.5 liter rotating autoclave. The initial hydrogen pressure was 70 atm. and the temperature 110-115°. The hydrogenation was completed after the absorption of approximately 23 liters of hydrogen (1.2 mole per mole of substance). After elimination of the catalyst by filtration, the dioxan was driven off under reduced pressure and the residue was vacuum distilled.

A fraction was obtained with a b.p. of 115-116° (3 mm), 87.3 g (71%) in weight.

d_4^{20} 1.1184; n_D^{20} 1.5032; MR_D 37.32; calculated 38.16.

0.1285 g sub.: 11.6 ml N_2 (22°, 741 mm). 0.1301 g sub.: 12 ml N_2 (21°, 747 mm). Found %: N 9.98, 10.2. $C_7H_{11}O_2N$. Calculated %: N 9.92.

* The molecular weight was determined in dioxan, since exaggerated results were obtained with the determination in benzene.

0.1873 g sub.: 16.03 g dioxan: Δt 0.38°. Found: M 145.2. $C_7H_{11}O_2N$. Calculated: M 141.16.

Furfurylaminoethanol with a b.p. of 113-116° (3 mm) was obtained in a yield of 43% by hydrogenation of furfurylidenaminoethanol in alcoholic solution with a platinum catalyst at atmospheric pressure and room temperature.

d_4^{20} 1.1120; n_D^{20} 1.5028; MR_D 37.51.

0.1442 g sub.: 13.2 ml N_2 (23°, 755 mm). 0.1993 g sub.: 18.2 ml N_2 (24°, 754.9 mm). 0.0197 g sub.: 7.2 ml CH_4 (22°, 760.8 mm). Found %: N 10.37, 10.26; active H 1.47. $C_7H_{11}O_2N$. Calculated %: N 9.92; active H 1.42.

Furfurylaminoethanol was also obtained by hydrogenation of furfurylidenaminoethanol in an autoclave in dioxan solution in the presence of nickel on kieselguhr (10% in relation to the weight of the substance); the initial hydrogen pressure was 105 atm, the temperature 120-130°. A product with a b.p. of 123° (6 mm); d_4^{20} 1.1110; n_D^{20} 1.5021; MR$_D$ 37.50. The yield was 50%.

Furfurylaminoethanol was a mobile, light yellow liquid with a weak amine odor and a sharp taste, which somewhat darkened during prolonged storage. It was quite soluble in water, alcohol, ether and acetic anhydride. It had an anesthetic action.

N-Acetofurfurylaminoethanol Acetate

8 g of furfurylaminoethanol and 30 g of acetic anhydride were placed in an assay autoclave, 50 ml in capacity; the autoclave was heated in a shaking tubular furnace for 1 hour to 200-220°. After the autoclave had cooled, the reaction mixture was extracted, the acetic anhydride and acetic acid driven off, and the residue vacuum distilled. 12 g (94%) of a light yellow liquid with a b.p. of 157° (2.5 mm) was obtained.

d_4^{20} 1.1614; n_D^{20} 1.4897; MR$_D$ 56.04; claculated 56.98.

0.1463 g sub.: 8.4 ml N_2 (26°, 759.5 mm). 0.1531 g sub.: 8.6 ml N_2 (22°, 741 mm). Found %: N 6.42, 6.21. $C_{11}H_{15}O_4N$. Calculated %: N 6.22.

There were no active hydrogen atoms present in the substance (as determined by Terentyev's method).

Acetofurfurylaminoethanol acetate is soluble in alcohol, acetic anhydride, benzene and dioxan.

Tetrahydrofurfurylaminoethanol

50.5 g of furfurylaminoethanol, 90 ml of dioxane and 4 g of NiK were placed in a rotating autoclave, 0.5 liter in capacity and hydrogenated at an initial hydrogen pressure of 94 atm and a temperature of 120-140°. The hydrogenation was concluded at an absorption of approximately 13.5 liters of H_2, which was equivalent to 1.55 mole per 1 mole of the substance.

By vacuum distilling the residue after elimination of the catalyst and solvent, 36.9 g of a basic fraction with a b.p. of 142-143° (23 mm) was obtained. The yield was 73.1%.

d_4^{20} 1.0780; n_D^{20} 1.4821; MR$_D$ 38.42; calculated 39.09.

0.1301 g sub.: 11 ml N_2 (21°, 764 mm). 0.1179 g sub.: 9.9 ml N_2 (22°, 747 mm). 0.0180 g sub.: 5.8 ml CH_4 (24°, 758 mm). Found %: N 9.68, 9.62; active H 1.27. $C_7H_{15}O_2N$. Calculated %: N 9.64; active H 1.38. 0.2005 g sub.: 17.53 g dioxan; Δt 0.36°. Found: M 149.6. $C_7H_{15}O_2N$. Calculated: M 145.19.

When 38 g of furfurylidenaminoethanol in anhydrous alcohol was hydrogenated with NiR at 150-160° and an initial hydrogen pressure of 120 atm, the hydrogenation was completed with the absorption of approximately 2.4 moles of H_2 per 1 mole of the substance. As a result of the 2-fold fractionation of the catalyzate in a vacuum, 18.54 g (48%) of tetrahydrofurfurylaminoethanol with a b.p. of 123-124° (4 mm) was obtained; there was a considerable quantity of resin in the residue.

d_4^{20} 1.0676; n_D^{20} 1.4812; MR$_D$ 38.72; calculated 39.09.

0.1182 g sub.: 0.2518 g CO_2; 0.1086 g H_2O. 0.1547 g sub.: 14 ml N_2 (25°, 757.5 mm). 0.1580 g sub.: 14 ml N_2 (24°, 755 mm). 0.0136 g sub.: 4.4 ml CH_4 (21°, 756.8 mm). Found %: C 58.11; H 10.28; N 10.09, 10.14; active H 1.30. $C_7H_{15}O_2N$. Calculated %: C 57.92; H 10.41; N 9.64; active H 1.38.

Tetrahydrofurfurylaminoethanol is a colorless liquid with a sharp taste, stable when stored. It is quite soluble in water, alcohol, benzene, dioxan, acetic anhydride and acetic acid; the pH of an aqueous solution is 9.0 (determined with a set of indicator papers).

Tetrahydrofurfurylaminoethanol forms characteristic precipitates with aqueous solutions of the salts of the divalent metals — for example, the precipitate with Cu^{++} ions is light brown, with Mn^{++} is light violet, etc..

N-Acetotetrahydrofurfurylaminoethanol Acetate

The acetylation was conducted in two assay autoclaves, 50 ml in capacity, into each of which 8 g of tetrahydrofurfurylaminoethanol, 30 g of acetic anhydride and 0.5 g of roasted $ZnCl_2$ were introduced. The autoclaves were heated in a shaking tubular furnace for 1.5 hoursat 170°. After eliminating the acetic anhydride and acetic acid, the residue was vacuum distilled, and 15.7 g of a yellowish liquid with a b.p. of 153° (2.5 mm); d_4^{20} 1.136; n_D^{20} 1.4780 was thereby obtained.

The substance was again vacuum distilled at 1.5 mm for analysis and had a b.p. of 149.5-150°.

d_4^{20} 1.1379; n_D^{20} 1.4792; MR_D 57.16; calculated 57.91.

0.1292 g sub.: 7.4 ml N_2 (24°, 744 mm). 0.1528 g sub.: 8.5 ml N_2 (27°, 751 mm). Found %: N 6.37, 6.21. $C_{11}H_{19}O_4N$. Calculated %: N 6.11.

0.1140 g sub.: 19.82 g benzene: Δt 0.14°. Found: M 211.2. $C_{11}H_{19}O_4N$. Calculated: M 229.26.

There were no active hydrogen atoms in the substance (Terentyev determination).

N-Acetotetrahydrofurfurylaminoethanol acetate is soluble in alcohol, dioxan, benzene, acetic anhydride and acetic acid.

Azomethine from Furylacrolein and Monoethanolamine

36.6 g of freshly distilled furylacrolein was dissolved in 30 ml of anhydrous alcohol, placed in a three-necked flask which was equipped with a mechanical stirrer and a separatory funnel, and 18.4 g of ethanolamine was added over a period of 2 hours while the mixture was carefully stirred. Under these conditions, a change in color and a small evolution of heat in the mixture were observed. The mixture was then stirred for 30 minutes more, while being heated on a water bath to 50°. The alcohol was distilled off under reduced pressure. 43 g of a fraction which boiled at 153-156° (3 mm) was removed by vacuum distillation; the yield was 86.8%. The yield of product reached 91% in other experiments. It consisted of a viscous, yellow colored liquid which rapidly darkened in air.

d_4^{20} 1.1194; n_D^{20} 1.6190; MR_D 51.79; calculated 46.00.

0.2795 g sub.: 17.2 ml 0.1 N H_2SO_4. 0.2183 g sub.: 13.5 ml 0.1 N H_2SO_4. Found %: N 8.61, 8.66. $C_9H_{11}O_2N$. Calculated %: N 8.48.

(α-Furylpropyl)-aminoethanol

43 g of freshly distilled azomethine was dissolved in 100 ml of anhydrous alcohol and hydrogenated in an 0.5 liter rotating autoclave in the presence of 4 g of Raney nickel at an initial hydrogen pressure of 109 atm and a temperature of 140-160°. The drop in pressure was equivalent to an absorption of approximately 2 moles of hydrogen per 1 mole of substance.

After elimination of the solvent and catalyst, the catalyzate was subjected to fractional distillation in a vacuum, as a result of which 18.3 g (41.5%) of a fraction with a b.p. of 134-135° (4.5 mm) was obtained.

d_4^{20} 1,0608; n_D^{20} 1.4970; MR_D 46.65; calculated 47.40.

0.2948 g sub.: 22 ml N_2 (21°, 755 mm). 0.3040 g sub.: 23.65 ml N_2 (25°, 764 mm). Found %: N 8.45, 8.75. $C_9H_{15}O_2N$. Calculated %: N 8.28. 0.1966 g sub.: 16.75 g dioxan: Δt 0.31°. Found: M 178.3. $C_9H_{15}O_2N$. Calculated: M 169.22.

The Verley method was used for the joint determination of the percentage content of the (NH + OH) groups.

0,3010 g sub.: 8.65 ml 0.5 N KOH (K = 0.8316). 0.2523 g sub.: 7.45 ml 0.5 N KOH (K = 0.8316). Found %: (OH + NH) 19.11, 19.64. $C_9H_{13}O$ (NH + OH). Calculated %: (OH + NH) 18.91.

N-Aceto-(α-furylpropyl)-aminoethanol Acetate

The acetylation was carried out in an assay autoclave at a temperature of 200° for 3 hours. 7.5 g of the amino alcohol, 1 g of roasted $ZnCl_2$ and 24 g of acetic anhydride were taken. The excess of acetic anhydride and acetic acid was distilled off; it was detected that about 8 g (2 equivalents) of acetic anhydride reacted. The residue was vacuum distilled and 7.6 g of a fraction with a b.p. of 152-165° (1 mm) was collected. As a result of a repeated distillation, 5.7 g of a thick liquid, which fluoresced in the freshly distilled state and had a b.p. of 165-168° (1 mm), was removed.

d_4^{20} 1.1196; n_D^{20} 1.4872; MR_D 65.09; calculated 66.22.

0.1109 g sub.: 0.0735 g H_2O; 0.2480 g CO_2. 0.1505 g sub.: 0.1024 g H_2O; 0.3392 g CO_2. 0.2108 g sub.: 11.6 ml N_2 (26°, 761 mm). 0.2459 g sub.: 13 ml N_2 (25°, 743 mm). Found %: C 61.23, 61.51; H 7.42, 7.55; N 6.15, 5.78. $C_{13}H_{19}O_4N$. Calculated %: C 61.52; H 7.56; N 5.53. 0.1470 g sub.: 17.73 g benzene: Δt 0.17°. 0.1612 g sub.: 18.24 g benzene: Δt 0.18°. Found: M 250.8, 252.4. $C_{13}H_{19}O_4N$. Calculated: M 253.3

In another experiment involving the hydrogenation of azomethine, which was carried out at an initial hydrogen pressure of 125 atm and 170°, 55 g of substance, 180 ml of dioxane and 7 g of NiR (12% in relation to the substance being hydrogenated) were taken. The hydrogen absorption calculated on the weight of the hydrogenated product was approximately equivalent to that required for the reduction of two double bonds. After eliminating the catalyst and distilling off the solvent, the residue was vacuum distilled at 1.5 mm. The following basic fractions were obtained: 1st fraction with a b.p. of 55-56°, n_D^{20} 1.4585, 2.2 g; 2nd fraction, b.p. 114-116°, n_D^{20} 1.4960, 9.65 g, and 3rd fraction, b.p. 172-174°, n_D^{20} 1.5492, 15.4 g.

The 1st fraction was again distilled at atmospheric pressure and boiled within the limits 164-168°; n_D^{20} 1.4570. The hydrochloride with a m.p. of 98-100° was obtained by passing dry HCl into a solution of the substance in anhydrous ether; it consisted of white crystals which deliquesced in air. On the basis of these data, it can be considered established that the substance was monoethanolamine (literature data: b.p. 169-171°, n_D^{20} 1.4539, hydrochloride – white crystals, m.p. 100°).

The 2nd fraction, as follows from its physical properties, was the previously described (α-furylpropyl)-aminoethanol.

d_4^{20} 1.06; n_D^{20} 1.4960; MR_D 46.6.

The 3rd fraction, as can be assumed on the basis of the data which follow below, was bis-(α-furylpropyl)-aminoethanol.

d_4^{20} 1.1370; n_D^{20} 1.5492; MR_D 77.61; calculated 78.57.

0.1542 g sub.: 0.1060 g H_2O; 0.3932 g CO_2. 0.1647 g sub.: 0.1123 g H_2O; 0.4198 g CO_2. 0.3192 g sub.: 16.2 ml N_2 (20°, 759 mm). 0.2854 g sub.: 13.9 ml N_2 (22°, 762 mm). 0.1484 g sub.: 12.8 ml CH_4 (24°, 762 mm). 0.1454 g sub.: 14.6 ml CH_4 (22°, 758 mm). Found %: C 69.59, 69.56; H 7.69, 7.63; N 5.8, 5.53; active H 0.34, 0.39. $C_{16}H_{23}O_3N$. Calculated %: C 69.3; H 8.29; N 5.05; active H 0.36. 0.3013 g sub.: 10.55 g benzene: Δt 0.534°. 0.3385 g sub.: 14.89 g benzene: Δt 0.425°. Found: M 274.9, 274.9. $C_{16}H_{23}O_3N$. Calculated: M 277.3.

The product was a very viscous liquid with a yellow color; was soluble in alcohol, ether, benzene, dioxan and in xylene on heating, and was insoluble in water.

SUMMARY

1. It was shown that furfural and β-(α-furyl)-acrolein react with monoethanolamine without catalyst, with the formation of the corresponding azomethines in excellent yields.

2. Experiments were described involving the hydrogenation under various conditions of the azomethines indicated above, as a result of which the following were obtained: furfurylaminoethanol, tetrahydrofurfurylaminoethanol, (α-furylpropyl)-aminoethanol and bis-(α-furylpropyl)-aminoethanol.

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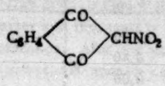
* See Consultants Bureau Translation, page 1811.

REACTION OF CERTAIN ALCOHOLS WITH 2-NITROINDANDIONE-1,3

E. Yu. Gudrinietse and G. Ya. Vanag

Several years ago, one of us with his coworkers showed [1] that 2-nitroindandione-1,3 (I) condenses very readily with benzhydrol to form 2-nitro-2-benzhydrylindandion-1,3 (II). Cleavage of the five-membered ring readily proceeds as a result of the action of aqueous or alcoholic alkali, and the unstable acid (III) is formed, which readily closes the ring again with formation of an isomeric product, the structure of which is still not entirely clear.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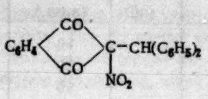
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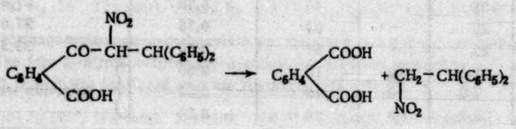
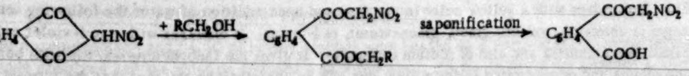

(III) (IV)

The more energetic action of alkali or alcoholate cleaves the phthalic acid with formation of benzhydrylnitromethane or β,β-diphenyl-α-nitroethane (IV). Thus, with the aid of nitroindandione, the nitromethyl group was successfully substituted for the hydroxyl group of benzhydrol as the end result of a series of readily-proceeding reactions

$$(C_6H_5)_2CHOH \rightarrow (C_6H_5)_2CHCH_2NO_2.$$

In order to determine to what extent this "nitromethylation" reaction with the aid of nitroindandione is general, the investigation was extended to other hydrols and often gave positive results.

L. Zalukaev investigated, simultaneously with these works, the reaction of methyl and ethyl alcohols with nitroindandione and found [2] that the reaction proceeds differently with these alcohols. These alcohols, analogously to alkalis or alcoholates, cleave the five-membered ring of nitroindandione with the formation of the esters of ω-nitroacetophenone-o-carboxylic acid (V). These esters are readily saponified and yield the free acid (VI), which has already been described in the literature:

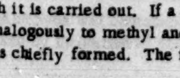


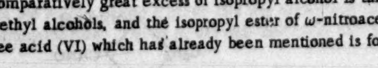
(V) (VI)

R = H or CH_3

It was of interest to investigate how other alcohols, above all, secondary aliphatic alcohols, would behave: would they react similarly to benzhydrol or similarly to methyl and ethyl alcohols?

Experiments set up with isopropyl alcohol showed that the course of the reaction depends on the conditions under which it is carried out. If a comparatively great excess of isopropyl alcohol is taken, then the reaction proceeds analogously to methyl and ethyl alcohols, and the isopropyl ester of ω-nitroacetophenone-o-carboxylic acid (VII) is chiefly formed. The free acid (VI) which has already been mentioned is formed by its saponification:


(VII)


(VIII)

The yields of the ester in general did not exceed 33% of the theoretical. Attempts to use ether, acetone, water, benzene and xylene as the solvent did not give positive results. When ethyl alcohol was used as the solvent, the ethyl ester of ω-nitroacetophenone-o-carboxylic acid (V,R = CH_3) was formed. However, the cleavage of the five-membered ring of nitroindandione and formation of the isopropyl ester of ω-nitroacetophenone-o-carboxylic acid proceeds in glacial acetic acid solution even when quite little isopropyl alcohol is taken. The ready cleavage of the indandione ring is a rather unusual phenomenon (in contrast to the cleavage of this ring in acidic medium by alcohol, which is a phenomenon generally known and described in the literature). Some results are given in the table.

TABLE

Expt. No.	Nitro-indan-dione (g)	Isopropyl alcohol (ml)	Glacial acetic acid (ml)	Duration of the heating (mins.)	Yield of isopropyl ω-nitroacetophenone-o-carboxylate (g)	in % of the nitroindandione
1	2.30	22	—	10	0.20	—
2	2.30	22	—	20	0.40	—
3	2.30	22	—	30	0.60	—
4	2.30	22	—	40	0.65	—
5	2.30	33	—	40	0.70	27.0
6	2.30	22	—	60	0.70	27.0
7	2.30	33	—	60	0.80	33.3
8	1.15	1.1	10	15	0.30	Together with resinous substances
9	1.15	2.2	5	15	0.30	
10	1.15	2.2	10	10	0.20	

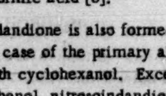
If considerably less isopropyl alcohol is taken (for example 20 ml of alcohol per 10 g of nitroindandione), the the reaction proceeds differently. The liquid becomes dark red colored and acetone is evolved. 2-Nitroso-indandione-1,3 (VIII) was isolated from the reaction products. It is evident that the nitroindandione here acts as an oxidizing agent which oxidizes the isopropyl alcohol to acetone, and is itself reduced to nitrosoindandione. A similar reaction was noted in due course with formic acid [3].

Careful investigation showed that nitrosoindandione is also formed by the reaction of nitroindandione with methy, ethyl, isobutyl and other alcohols. In the case of the primary alcohols, however, the yields of nitrosoindandione are very small. They are also small with cyclohexanol. Excellent yields of nitrosoindandione are obtained with benzyl alcohol (72.9%); with acenaphthenol, nitrosoindandione was obtained in a yield of 82.9%.

The properties of nitrosoindandione have been very scantily described in the literature [3, 4]; it was thus not easy to recognize it at once and the nitrosoindandione obtained was, consequently, studied in somewhat greater detail.

It is insoluble in ether and cold water; difficultly soluble in chloroform; more soluble in hot water, hot alcohol, glacial acetic acid. It dissolves with a yellow color in pyridine and upon addition of water the following sequence of color changes is observed: yellow, green, green-violet, red-violet. It dissolves with a red-violet color in solutions of alkali and ammonia and also of sodium carbonate. It gives the indophenine reaction with benzene which contains thiophene and concentrated sulfuric acid; this can be explained by the fact that the nitrosoindandione is partially converted into indantrione oxime which is cleaved to indantrione, and the latter, as experiments have shown, actually gives the indophenine reaction. It is characteristic, however, that nitrosoindandione itself can not be cleaved [5] to indantrione (ninhydrin), which is evidence in favor of the nitroso form [3]. On heating with 10% sodium hydroxide, phthalic acid and sodium cyanide are formed.

2,2-Dibromindandione-1,3 is formed by the action of bromine on nitrosoindandione. The bis-phenylhydrazone (IX) is formed with phenylhydrazine:



(IX)

It has already been noted in due course [3], that the melting point of nitrosoindandione depends on the speed of heating the substance. It proved also to be dependent on the solvent from which the nitrosoindandione was recrystallized. Thus, for example, on heating nitrosoindandione under as identical conditions as possible, it melted at 216-218° when recrystallized from glacial acetic acid, at 204-206° when crystallized from water, at 215-216° after a secondary crystallization from glacial acetic acid, and at 201-202° after a secondary crystallization from water. It is possible that both tautomeric forms (VIII), are formed here. The question was not investigated in greater detail.

EXPERIMENTAL

Isopropyl ω-Nitroacetophenone-o-carboxylate (VII)

2.3 g of nitroindandione and 33 ml of isopropyl alcohol were heated on a water bath for approximately 1 hour. The nitroindandione gradually dissolved and the liquid began to assume a dark red color. When the reaction was terminated at this moment, the best yields were obtained. After cooling, the solution, it was diluted with a 5-10 fold quantity of water. Needle-like crystals then precipitated together with a small amount of an oily substance, which was readily soluble in ether and thus readily separable. This oily product was dissolved in concentrated sulfuric acid with a green fluorescence. After the ether treatment, the residue was recrystallized from acetic acid (1:1) and 0.8 g of isopropyl ω-nitroacetophenone-o-carboxylate was obtained, which amounted to 33.3% of the theoretical. The m.p. was 70-71°.

4.114 mg sub.: 0.222 ml N_2 (20°, 764 mm). Found %: N 6.01. $C_{12}H_{11}O_4N$. Calculated %: N 6.32.

When the isopropyl ω-nitroacetophenone-o-carboxylate was dissolved in 2.0 N sodium hydroxide, saponification of the ester occurred. The free ω-nitroacetophenone-o-carboxylic acid was isolated by acidifying the solution. The m.p. was 122-123°, which was in accord with the literature data (121.5°).

3.400 mg sub.: 0.194 ml N_2 (21°, 754 mm). Found %: N 6.57. $C_9H_7O_5N$. Calculated %: N 6.72.

Isobutyl (Primary) ω-Nitroacetophenone-o-carboyxlate (V, R=$CH(CH_3)_2$)

It was obtained analogously to the preceding. The m.p. was 89-90°.

4.200 mg sub.: 0.198 ml N_2(20°, 749 mm). Found %: N 5.42. $C_{13}H_{13}O_4N$. Calculated %: N 5.67.

Reduction of Nitroindandione with Isopropyl Alcohol

10 g of nitroindandione and 20 ml of isopropyl alcohol were heated on a water bath for 2 hours. The solution became dark red in color and acetone was evolved: a paper, moistened with o-nitrobenzaldehyde and alkali, became blue colored when held in the vapors with the formation of indigo. The reaction liquid was diluted with an approximately 5-fold quantity of water. A yellow crystalline precipitate settled out together with an oily substance. After treatment with ether and crystallization from glacial acetic acid, 2 g of the nitrosoindandione (VIII) was obtained which amounted to 28.6% of the theoretical. The m.p. was 217-218°.

3.886, 3.271 mg sub.: 0.270 ml N_2 (22°, 752 mm), 0.225 ml N_2 (18°, 758 mm). Found %: N 8.14, 8.05. $C_9H_5O_3N$. Calculated %: N 8.00.

Reduction of Nitroindandione with Benzyl Alcohol

12 g of nitroindandione and 24 ml of benzyl alcohol were heated on a water bath. In about 20 minutes the nitroindandione dissolved and the solution assumed a dark red color. In the course of 30 minutes, a vigorous reaction occurred and yellow crystals appeared. The yield of 6.8 g of nitrosoindandione (VIII) amounted to 68.3% of the theoretical. The reddish-brown filtrate was shaken with 10% sodium carbonate solution, the aqueous layer was separated and acidified. Needle-like green crystals of nitrosoindandione precipitated. After crystallization from glacial acetic acid, the m.p. was 216-217° and after crystallization from water, it was 208-212°. The total yield of nitrosoindandione was 7.3 g (72.9%).

2.386 mg sub.: 0.162 ml N_2 (19°, 747 mm). Found %: N 7.80. $C_9H_5O_3N$. Calculated %: N 8.00.

Benzaldehyde was contained in the reddish-brown filtrate; this was shown both by qualitative reactions for aldehydes and by formation of the semicarbazone. The m.p. was 225-228° (222, 227° according to the literature data).

2.743 mg sub.: 0.613 ml N_2 (21°, 764 mm). Found %: N 26.08. $C_8H_9ON_3$. Calculated %: N 25.76.

Reduction of Nitroindandione with Acenaphthenol

2.3 g of nitroindandione, 2.6 g of acenaphthenol and 15 ml of glacial acetic acid were heated to boiling for 5-10 minutes. A vigorous reaction occurred and a yellow precipitate of nitrosoindandione was formed. The yield of 1.6 g amounted to 82.9% of the theoretical. It was not different in its properties from the nitrosoindandione described above.

2.886 mg sub.: 0.200 ml N_2 (22°, 760 mm). Found %: N 8.02. $C_9H_5O_3N$. Calculated %: N 8.00.

2,2-Dibromindandione from Nitrosoindandione

1.5 g of nitrosoindandione was drenched with excess bromine water. The yellow nitrosoindandione was converted into the white 2,2-dibromindandione-1,3 which was insoluble in water. After crystallization from glacial acetic acid, the m.p. was 178°, which was in accord with the literature data. A mixture with known 2,2-dibromindandione displayed no melting point depression.

Bis-phenylhydrazone of Nitrosoindandione (IX)

2 g of nitrosoindandione in aqueous solution was heated with an aqueous solution of 5 g of phenylhydrazine hydrochloride. A flocculent, dark red precipitate was quickly formed. After crystallization from dilute ethyl alcohol, orange needles of the bis-phenylhydrazone with a m.p. of 201° were obtained.

3.729 mg sub.: 0.637 ml N_2 (18°, 758 mm). 4.057 mg sub.: 0.696 ml N_2 (19°, 759 mm). Found %: N 19.99, 20.03. $C_{21}H_{17}ON_5$. Calculated %: N 19.71.

SUMMARY

On heating nitroindandione with a large excess of isopropyl or primary isobutyl alcohol, cleavage of the five-membered ring of nitroindandione occurs and the corresponding ester of ω-nitroacetophenone-o-carboxylic acid is formed.

On heating nitroindandione with a small excess of isopropyl or benzyl alcohol, and also with acenaphthenol, oxidation of these alcohols into the corresponding aldehyde or ketone occurs, while the nitroindandione is reduced to nitrosoindandione. The properties of this last compound were studied in greater detail.

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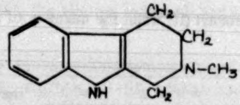
* See Consultants Bureau Translation, page 1543.

INVESTIGATION OF THE PRODUCTS OF THE CONDENSATION OF N-METHYLTRYPTAMINE WITH FORMALDEHYDE

N. K. Yurashevsky*

With the object of investigating the mechanism of the reciprocal reaction of derivatives of 2,3,4,5-tetrahydro-3-carboline with acid chlorides, we undertook the preparation of several bases of this group, including 3-methyl-2,3,4,5-tetrahydro-3-carboline (also known as N-methyltetrahydronorharmane) (I):

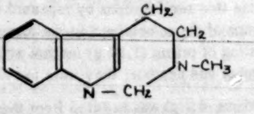


(I)

Having acquired a sufficient supply of N-methyltryptamine, we naturally determined to prepare the above-mentioned compound via the condensation of N-methyltryptamine with formaldehyde by analogy with the well-known method of preparing other derivatives of 2,3,4,5-tetrahydro-3-carboline and also of tetrahydroisoquinoline.

In the condensation, which we brought about under the conditions described by Akabori [1], we completely unexpectedly obtained, however, a mixture of three bases, two of which had the elementary composition and molecular weight which corresponded to those of N-methyltetrahydronorharmane, i.e., $C_{12}H_{14}N_2$, and the third, to those of the empirical formula $C_{13}H_{16}ON_2$. In the investigation of the properties of the bases obtained, it turned out that both isomeric $C_{12}H_{14}N_2$ compounds were monoacidic bases, and the nitrogen atom, to which the basic properties were due, was of a tertiary nature and was included in the ring, since in a Hofmann degradation of the iodomethylates of both bases, the trimethylamine was formed only in the second stage. The two isomers were markedly different in the fact that one of them, the isomer with a m.p. of 225-226°, was incapable of reacting with nitrous acid, while the other (with a m.p. of 217-218°) yielded a nitrosocompound but, however, retained a basic character and on heating with acids was readily reconverted into the initial substance. This observation permitted the solution of the problem of determining which of the two isomeric bases was N-methyltetrahydronorharmane (I), in favor of the base with a m.p. of 217-218°.

For the second isomer with a m.p. of 225-226°, formula (II) seemed uniquely possible to us, since it satisfactorily explained not only the properties of this compound



which had been described before, but also the fact that it is formed in the condensation of N-methyltryptamine with formaldehyde.

The structure of the third compound of composition $C_{13}H_{16}ON_2$ was established on the basis of the observation that on heating the base above its melting point, the substance splits off a molecule of formaldehyde and is converted into a base with a m.p. of 217-218° which proved to be identical with N-methyltetrahydronorharmane (I). This behavior of the base with the composition $C_{13}H_{16}ON_2$ is readily explained by formula (III):

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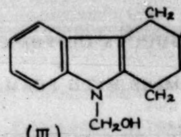

(III)

We assumed that this last substance (1-hydroxymethyl-3-methyl-2,3,4,5-tetrahydro-3-carboline or alternatively N(py)-methyl-N(ind)-hydroxymethyltetrahydronorharmane) is a secondary product of the reaction and, specifically, can be formed only in the presence of a sufficient excess of formaldehyde via the condensation of N-methyltetrahydronorharmane with a new molecule of formaldehyde. It consequently, seemed to us to be not without interest to investigate how the yield of condensation products changes depending on the quantity of formaldehyde taken for the reaction. The results, which completely confirmed our assumptions, are presented in the table.

The marked reduction in the yield of product (II) when the quantity of formaldehyde is equivalent to the theoretical amount, is not entirely clear.

TABLE

Quantity of moles of formaldehyde per mole of N-methyltryptamine	Yield (%)		
	N-methyltetrahydronorharmane (I)	N(py)-methyl-N(ind)-hydroxymethyltetrahydronorharmane (III)	Base (II).
6	–	57	14
2	23	41	12
1	78	–	2

It seems possible to us to explain the cause of the lowered yield of 2,3,4,5-tetrahydro-3-carboline in the condensation of tryptamine with formaldehyde in the case of an excess of the latter as Spāth reports concerning this [2], in connection with the results obtained.

Tetrahydronorharmane, which has, in comparison with N-methyltetrahydronorharmane, not only an extra, but also more active hydrogen atoms, naturally exhibits to a much greater extent a tendency toward the formation of secondary condensation products in the presence of the excess aldehyde which, on account of side reactions, is ordinarily taken in a quantity several times greater than is theoretically required.

EXPERIMENTAL

17 ml of H_2O and 8 ml of a 35% solution of formalin (2.8 g of the aldehyde) was added to a solution of 8 g of N-methyltryptamine in 95.1 ml of 0.5 N H_2SO_4. The solution was slowly heated on an oil bath to 110° and this temperature was maintained for 20 minutes. The cooled solution was rendered alkaline with KOH, extracted with chloroform and the chloroform extract treated with 10% H_2SO_4.

After the addition of excess alkali to the acid solution, the base was extracted with ether. 3 fractions of crystals with m.p. of 208-211, 180-188 and 133-136° were isolated from the ethereal solution by fractional crystallization. Two bases were isolated from the first two fractions by repeated recrystallization from acetone, or better, from a mixture of benzene and alcohol; one of these, obtained in the form of fluffy flakes and needles, had a m.p. of 217-218° (2 g), while the other, consisting of prisms (1.02 g) melted at 225-226°. Both bases were completely colorless and poorly soluble in ether, alcohol and acetone; they were not soluble in water.

A base with a m.p. of 140-141° (prisms, 4.1 g) was isolated from the third fraction of crystals with a m.p. of 133-137° by recrystallization from ether, and proved to be the chief constituent part of this fraction.

Base with a M.p. of 217-218° (I)

0.0742, 0.0702 g sub.: 0.2104, 0.1986 g CO_2; 0.0498, 0.0484 g H_2O. 0.0664, 0.0738 g sub.: 8.85 ml N_2 (17.5°, 753 mm); 9.8 ml N_2 (17.5°, 751 mm). 0.0144 g sub.: 20.1072 g benzene: Δt 0.020° (average of 3 determinations). 0.0196 g sub.: 0.2282 g camphor: Δt 20.5°. Found %: C 77.35, 77.15; H 7.51, 7.73; N 15.2, 15.11; M 183 (by Beckmann's method), 167.5 (by Rast's method). $C_{12}H_{14}N_2$. Calculated %: C 77.36; H 7.58; N 15.05; M 186.

Hydrochloride. It was prepared by dissolving the base in an alcoholic solution of HCl. After adding a small quantity of ether, crystals were rapidly formed in the form of fine, snow-white needles with a m.p. of 247-248°.

Picrates. Depending on the quantity of picric acid, either the yellow mono-, or the red dipicrate can be obtained. The latter crystallizes (from alcohol) only in the presence of a large excess of picric acid, and when it is recrystallized in the absence of free picric acid, a mixture of the mono- and dipicrates crystallizes out. The melting point of the dipicrate is 175-176°, of the monopicrate, 195-196°. A mixed sample melted at 155-165°.

Analysis of the dipicrate with a m.p. of 175-176°: 0.0832, 0.0904 g sub.: 0.1362, 0.1478 g CO_2; 0.0228, 0.0258 g H_2O. Found %: C 44.64, 44.59; H 3.06, 3.19. $C_{12}H_{14}N_2 \cdot (C_6H_3O_7N_3)_2$. Calculated %: C 44.7; H 3.12.

Nitroso compound. A 10% nitrite solution was gradually added to 0.2 g of the base in 5% H_2SO_4 while it was being cooled. The solution thereupon became yellow, but remained transparent. After the addition of excess alkali, the yellow precipitate which settled out was treated with ether and the ethereal solution was concentrated. A yellow oil remained in the residue which clearly reproduced the Liebermann reaction and was quite soluble in acids. The nitroso product obtained was dissolved in 5 ml of acetone and converted into the picrate by the addition of an acetone solution of picric acid. Almost at once the crystallization of the picrate began; the picrate was poorly soluble in cold acetone. The decomposition temperature was 210-211° (it preliminarily darkened and shrank at about 196-197°). The picrate reproduced the Liebermann reaction. On heating the alcoholic solution of the picrate with excess picric acid, the solution reddened, and after cooling, the dipicrate of the initial base crystallized out.

Analysis of the picrate with a decomposition temperature of 210-211°: 0.0766 g sub.: 12.8 ml N_2 (19°, 757 mm). Found %: N 19.03. $C_{12}H_{13}N_2NO \cdot (C_6H_3O_7N_3)$. Calculated %: N 18.92.

Iodomethylate. 0.4 g of the base was dissolved in a mixture of 10 ml of methanol and 1 ml of CH_3I. The iodomethylate thereupon quickly began to crystallize; after recrystallization from methanol it had a m.p. of 257-258°. The yield was 0.67 g.

Hofmann degradation of the iodomethylate. A solution of 0.6 g of the iodomethylate and 5 g of KOH in 35 ml of methanol was heated for 5 hours on a water bath. The evolution of trimethylamine was not observed. The methyl alcohol was driven off on a water bath and the residue was treated with ether. After eliminating the ether, the degraded base was left in the form of a yellow oil. The iodomethylate obtained from it in the usual way, in contrast to the initial iodomethylate, was quite soluble in methanol. On heating the iodomethylate of the degraded base in an alcoholic KOH solution, the odor of trimethylamine quickly became clearly perceptible.

Base with a M.p. of 225-226° (II)

0.0930, 0.0724 g sub.: 0.2630, 0.2054 g CO_2; 0.0618, 0.0484 g H_2O. 0.0848, 0.0816 g sub.: 10.95 ml N_2 (17°, 770 mm), 10.7 ml N_2 (18°, 768 mm). 0.0252 g sub.: 20.2586 g benzene: Δt 0.033° (average of 3 determinations). 0.0062 g sub.: 0.1476 g camphor: Δt 9.5°. Found %: C 77.13, 77.37; H 7.43, 7.47; N 15.09, 15.23; M 193 (by Beckmann's method), 177 (by Rast's method). $C_{12}H_{14}N_2$. Calculated %: C 77.36; H 7.58; N 15.05; M 186.

Picrate. Upon addition of picric acid to a solution of the base in acetone, a crystalline yellow precipitate of the picrate at once settled out, which was very poorly soluble in the usual organic solvents and almost completely insoluble in water. The m.p. was 237-238°. The same picrate was formed in the presence of insufficient picric acid, as in the presence of a large excess of it.

Picrolonate. It consisted of a finely crystalline yellow precipitate which was very poorly soluble even in hot acetone; decomposition temperature, 223°.

Iodomethylate. 0.3 g of the base was dissolved in a mixture of 10 ml of methanol and 1 ml of methyl iodide; the crystallization of the iodomethylate in the form of clumps of fine needles, which were very poorly soluble in alcohol, thereupon quickly began; the m.p. was 272-273° (with decomposition).

Hofmann degradation of the iodomethylate. 0.3 g of the iodomethylate together with 40 ml of a 15% solution of KOH in methanol was heated for 8 hours on a water bath. The odor of trimethylamine was not perceived. The degraded base which was isolated by direct extraction with ether was converted into the iodomethylate; the latter gradually darkened on heating and at 187-188° became completely black. Further increase in the temperature even to 250° did not cause an appreciable change in the substance. On heating the iodomethylate of the degraded base in an alcoholic solution of potassium hydroxide, the odor of trimethylamine was quickly clearly perceptible. After heating for 6 hours, the methyl alcohol was driven off, and the residue was diluted with water and subjected to extraction with ether. The ethereal solution was shaken with a 2% solution of H_2SO_4 and then dried with potash. The residue after the ether had been eliminated quickly crystallized out. The substance obtained, neutral to litmus, was poorly soluble in alcohol and quite soluble in benzene. The m.p. was 151-152°. It reproduced the Ehrlich reaction, but only on heating. As a consequence of the insufficient amount of the substance, the elementary analysis was not carried out.

Attempt at nitrosation. Nitrite solution was gradually added to an ice-cooled solution of 0.2 g of the base in 5% H_2SO_4. The liquid remained transparent under these conditions. After the solution had been rendered alkaline, the product was extracted with ether and proved to be the initial base.

Base with a M.p. of 140-141° (III)

0.0962, 0.0834 g sub.: 0.2550, 0.2206 g CO_2; 0.0652, 0.0556 g H_2O. 0.0992, 0.0978 g sub.: 11.4 ml N_2 (18°, 751 mm), 11.35 ml N_2 (18°, 751 mm). Found %: C 72.28, 72.14; H 7.58; 7.46; N 13.05, 13.18. $C_{13}H_{16}ON_2$. Calculated %: C 72.18; H 7.46; N 12.96.

Hydrochloride. After the base had been dissolved in an alcoholic HCl solution, crystallization of the hydrochloride began almost at once; it was poorly soluble in cold alcohol. The m.p. was 198° (with decomposition).

Picrate. It consisted of yellow needles which were very poorly soluble in alcohol and melted at 191-192°.

The base dissolved quite well in the usual organic solvents. When the base was fused, the evolution of gas bubbles occurred, after which the substance once more hardened and melted again at 211-213°.

With the object of elucidating the chemistry of this conversion, 0.3 g of the base was heated to 160° for 5 minutes in a test tube on an oil bath. The gaseous substance which was evolved during the heating proved to be formaldehyde, the sharp odor of which was perceived only a few seconds after the beginning of the heating. The thickening substance melted at 217-218° after recrystallization from acetone. The substance proved to be identical with the base which had a m.p. of 217-218°. A mixed sample melted at the same temperature.

Experiments involving the condensation of N-methyltryptamine with the theoretical, and with a six-fold, quantity of formaldehyde were carried out under conditions which were analogous to those described above. The yields of the separate condensation products are presented in the table which appears in the theoretical part of this article.

SUMMARY

1. In the reaction of N-methyltryptamine with formaldehyde, in addition to the fundamental reaction which leads to the synthesis of 3-methyl-2,3,4,5-tetrahydro-3-carboline, there also occurs the condensation of a formaldehyde molecule with the two nitrogen atoms of N-methyltryptamine with the formation of a seven-membered ring.

2. In the presence of excess formaldehyde, the 3-methyl-2,3,4,5-tetrahydro-3-carboline, in adding a second molecule of formaldehyde, is converted into 1-hydroxymethyl-3-methyl-2,3,4,5-tetrahydro-3-carboline.

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INVESTIGATION OF THE DELPHINIUM ALKALOIDS

VI. THE N-ALKYL GROUP OF DELSINE

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As is well-known, one of the characteristic peculiarities of the aconitic alkaloids consists in the fact that to a considerable extent their nitrogen is alkylated with the ethyl radical. Several years ago, this interesting fact was almost simultaneously noted by three groups of investigators [1, 2, 3], and although it subsequently was the basis of many works on the aconitines, it, however, still remains disputable.

The character of the N-alkyl group in the aconitine series of alkaloids is judged by the following signs:

a) When the alkaloid is fused with alkalis, methylamine or ethylamine is, respectively, detected in the volatile products of dry distillation which are characterized most simply by the picrates [1, 2, 3];

b) In a well-known method of determining the alkoxy and alkylimide groups, when they are both present, the methoxy groups of the alkaloid are initially saponified with hydriodic acid, and then the alkyl group is split off from the nitrogen; the alkyl iodide formed is trapped with a trimethylamine solution and identified in the form of the iodide of tetramethylammonium or triethylammonium [1, 2, 3].

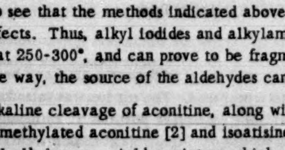
c) When oxidized with permanganate in sulfuric acid solution the aconitine alkaloids, depending on the character of the N-alkyl group, split off formaldehyde or acetaldehyde; either of these aldehydes is readily determined in the form of the condensation product with dimedone [3, 4, 6].

It is not difficult to see that the methods indicated above, in spite of their apparent objectivity, are also not free of substantial defects. Thus, alkyl iodides and alkylamines are products of the pyrogenetic reactions which are brought about at 250-300°, and can prove to be fragments of the more important portions of the molecule. In exactly the same way, the source of the aldehydes can equally be a different kind of C-alkyl grouping.

Actually, in the alkaline cleavage of aconitine, along with ethylamine, a small quantity of methylamine [3] is always formed. Demethylated aconitine [2] and isoatisine [5], under conditions which are appropriate for the determination of an N-alkyl group, yield a mixture which consists of ethyl iodide and an appreciable quantity of methyl iodide. In certain oxo-derivatives, the alkylimidic group in general does not submit even to qualitative determination [7, 8, 9]. It is, consequently, not accidental that the question of the character of the N-alkyl group of the aconitines has remained in dispute up to the present time [10]. Not only the presence of an N-ethyl group, but in general, the very presence of any alkyl group on the nitrogen atom, has been questioned [7, 9]. It is assumed that "it is possible that the so-called N-alkyl groupis actually only a rather labile C-alkyl group", or "this alkyl group acts as a connecting link between the nitrogen atom and the rest of the molecule" [8]. Finally, Jacobs [11] recently expressed the opinion that the nitrogen in atisine is alkylated with a hydroxyethyl group $>N-CH_2-CH_2OH$. No experimental data in support of this hypothesis were adduced.

Since many questions are closely linked with the character of the N-alkyl group, which concern the structure of the series of alkaloids under consideration, we have undertaken several new investigations in this direction.

As has already been described [12], to elucidate the attachment of the N-alkyl group of the alkaloid delsine, the latter was subjected to oxidation with potassium permanganate; acetaldehyde was thereupon detected, on the basis of which delsine was classified as an alkaloid which contains an ethyl group on the nitrogen. Experimental



data are cited in the present article, which completely confirms this hypothesis.

We have succeeded in bringing about the partial cleavage and resynthesis of the alkaloid. Under the oxidizing action of excess nitrous acid, the nitrogen alkyl group was eliminated from delsin , which led to the formation of the nitroso compound (II). The product obtained by reduction in an alcoholic solution of hydrochloric acid was converted into the free nor-base (III). The secondary character of base (III) was confirmed by the fact that it readily yields back the initial nitroso compound (II) with dilute nitrous acid. The nor-base of delsine was in turn alkylated with methyl iodide and ethyl iodide. The product of the first reaction (IV) proved to be distinct in its physico-chemical constants from delsine. A compound which was completely identical with the hydriodide of delsine was obtained by alkylating the nor-base with ethyl iodide.

A special experiment was set up to elucidate the character of the oxidizing action of potassium permanganate on nordelsine. As was not strange, even without an alkyl group at the nitrogen, the base proved to be still capable of splitting off aldehyde, although this time, for some reason, it is formaldehyde. It is necessary to assume that the fact, which has long been well-known, that aldehydes are formed in the oxidation of aconitine alkaloids is evidently associated not only with the presence of alkylated nitrogen atoms, but also with the presence of other elements making up the structure of the molecule which readily yield to oxidation.

In the first communication on the discovery of delsine [12], the reservation was made that this alkaloid in certain of its properties resembles the amino alcohol lycotonine, but differs from it in the character of the substituent groups and the melting points of its salts. Several new works on lycotonine have appeared in subsequent years [10, 13, 14, 15]. The corrected constants of lycotonine are identical in the majority of cases with the data previously indicated by us for delsine. The formula $C_{25}H_{41}O_7N \cdot H_2O$ is also acknowledged as the most reliable [10]. At the present time there remains almost no doubt relative to the identity of both bases. The presence of lycotonine – delsine has been definitely established in 9 forms of Delphinium (D. ajacis, D. barbeyi, D. brownii, D. consolida, D. elatum, D. oreophilum, D. rotundifolium, D. semibarbatum, D. sp) and only in one of the species of Aconitum (A. lycoctonum). Evidently, this is one of the most widely distributed alkaloids among the plants of the genus Delphinium; consequently, the name "delsine" more fully reflects the generic relation of the alkaloid with the plants which produce it. For this reason, the name "delsemidine" should be preferred to the name "methyllycaconitine".

EXPERIMENTAL

N-Nitrosonordelsine

Preparation. 10.0 g of delsine was dissolved in 400 ml of 25% acetic acid and heated on a water bath. 100 ml of a 60% solution of sodium nitrite was separately prepared. The nitrite was introduced into the reaction mixture in equal portions of 25 ml: the first portion at once, the other portions at 15 minute intervals. After the last portion had been added, the heating was continued for 1 hour more. The cooled solution was neutralized with sodium carbonate and extracted with chloroform. The chloroform solution was concentrated to small volume. The residue was freed from the chloroform by subsequent concentration in air of alcohol and water solutions. After 2-3 days in a concentrated water solution, a crystalline precipitate of nitrosonordelsine began to settle out. The yield was 2.1 g. The bulk of the alkaloid which had reacted was left in the water-alkali solution in the form of an amphoteric compound. The latter displayed a positive reaction with silicotungstic acid, but did not dissolve in organic solvents.

In another experiment a solution of 4.0 g of delsine in 160 ml of 5% sulfuric acid was treated under analogous conditions with 40 ml of a 30% solution of $NaNO_2$. As a result, 2.6 g of delsine was recovered and only 0.25 g of nitrosonordelsine was isolated. We did not succeed in increasing the yield of the nitroso product above 20-22%.

Properties. For recrystallization, the nitroso compound was dissolved in a small quantity of alcohol; the solution was diluted with water and slowly concentrated in air. After it had been twice recrystallized in a similar fashion, the substance formed long, colorless, needle-like crystals with a m.p. of 79-80°* $[\alpha]^{16}_{D} -50.7°$ (c 2.38 in ethanol). On heating, and also on standing in a vacuum desiccator over $CaCl_2$, the crystals acquired a dull tinge, which was associated with the loss of four molecules of water of crystallization.

Found %: H_2O 13.44, 13.61. $C_{23}H_{36}O_8N_2 \cdot 4H_2O$. Calculated %: H_2O 13.33.

The dried product had no sharp melting point. It began to sinter at 124°, and the substance finally softened at 128°, but even at 135° no clear meniscus was yet observable: $[\alpha]^{16}_{D} -59.5°$ (c 2.00 in ethanol).

Found %: C 58.68, 58.72; H 7.92, 7.79; N 5.87, 5.92; OCH_3 26.28, 26.36. $C_{23}H_{36}O_8N_2$. Calculated %: C 58.96; H 7.74; N 5.98; $4OCH_3$ 26.49.

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* All the melting points given in the text are corrected.

The analysis for methoxy groups was hampered due to the instantaneous evolution of iodine. The substance showed an appreciable reaction for the nitroso group with phenol and sulfuric acid. The nitrosonordelsine was not precipitated from acidified solutions by silicotungstic acid, although it still retained certain weakly basic properties.

The hydrobromide of nitrosonordelsine was isolated in the form of coarse prisms by adding dry ether to an alcoholic solution of the nitroso product which was acidified with hydrobromic acid. After recrystallization from a mixture of alcohol and ether, it had a m.p. of 187-188° (decomposition).

The chlorate of nitrosonordelsine was precipitated in an analogous fashion with ether from an alcoholic solution of the nitroso compound which was acidified with chloric acid. The dried salt melted at 188° (with decomposition).

A small quantity of the salt was treated with ammonia and the nitrosamine which was freed was extracted with chloroform. The chloroform was evaporated off, and the residue was recrystallized from water. The crystals thereby obtained had a m.p. of 77-79° and a mixed sample with nitrosonordelsine displayed no melting point depression.

Nordelsine

Preparation. The nitrosamine was not reduced in the presence of platinum black either in alcoholic or in acetic acid solution, even when the temperature was raised.

1.75 g of the anhydrous nitrosonordelsine was dissolved in 25 ml of anhydrous alcohol, and the solution was saturated with hydrogen chloride while being cooled externally to −10°. The reaction mixture was kept for 3 days in a sealed tube at room temperature, and then was concentrated in a vacuum. The residue was dissolved in 20 ml of water and after neutralization (to the point at which gas bubbles were no longer evolved) with sodium carbonate, it was repeatedly extracted with chloroform (for the neutral reaction products). The aqueous solution was then rendered strongly alkaline with ammonia, and the basic reaction products were extracted with chloroform. The chloroform solution was concentrated to small volume. At the end, several milliliters of water were added to the flask to be distilled off, and the heating was continued until no chloroform odor was present and the reaction product did not dissolve in water. The aqueous solution was filtered and concentrated on a water bath. The residue was dried in a vacuum desiccator over calcium chloride. The yield of nor-base was 1.16 g.

The chloroform solution which contained the neutral reaction products was treated in exactly the same way and gave 0.36 g of a brownish amorphous mass.

Properties. Nordelsine consists of a vitreous substance of a yellowish color, and is readily converted into an amorphous powder on grinding. It is quite soluble in water. We did not succeed in crystallizing the base from any solvent or in obtaining its crystalline salts. Nordelsine begins to sinter at approximately 80° and melts at 102-104°; $[\alpha]^{25}_{D}$ + 54.1° (c 5.19 in ethanol for the dehydrated substance). The substance attracts moisture in air which is eliminated without difficulty in a vacuum. One molecule of water, however, is strongly held by the base and is evolved with foaming only at the melting point.

Found %: C 62.65, 62.57; H 8.64, 8.71; N 3.24, 3.31; H_2O 4.24. $C_{23}H_{37}O_7N$. Calculated %: C 62.85; H 8.48; N 3.19; H_2O 3.94.

Nordelsine and HNO_2. 0.2 g of nordelsine was dissolved in 10 ml of 10% sulfuric acid and treated with 3 ml of a saturated solution of sodium nitrite. The reaction mixture was left for a day at room temperature. On the following day, the solution was rendered alkaline with ammonia and extracted with chloroform. The chloroform was driven off and the residue (0.17 g) was twice recrystallized from water. The crystals obtained, with a m.p. of 79-80°, $[\alpha]^{18}_{D}$ − 51.3° (c 2.02 in ethanol), were completely identical with nitrosonordelsine.

Oxidation of nordelsine. 0.40 g of $KMnO_4$ in 10 ml of water was added over a period of 2 hours to a cooled solution of 0.41 g of nordelsine in 10 ml of 5% sulfuric acid which was being stirred. After the solution had become colorless, the manganese dioxide precipitate was filtered off, and the filtrate was distilled into a well-cooled receiving vessel. 20 ml of a 1% aqueous solution of dimedon was added to the distillate obtained, which had an acid reaction. The mixture was heated for several minutes on a boiling water bath; turbidity thereupon appeared which was converted into a finely crystalline precipitate. The yield was 12 mg. After recrystallization from dilute alcohol, the crystals had a m.p. of 188°. A mixed sample with the product of the condensation of dimedon with formaldehyde melted at 187-188°.

N-Methylnordelsine

Preparation. 0.55 g of nordelsine was dissolved in 8 ml of methanol, stirred with 0.5 ml of methyl iodide and heated in a sealed tube on a water bath for 2 hours. The excess of methyl iodide and methanol was evaporated off and the solution concentrated to small volume (1.5-2 ml). Ether (6-8 ml) was poured into the cooled solution along the walls. After some time, needle-like crystals of methyl-nordelsine hydriodide began to grow at the boundary of the two layers. The salt obtained was dissolved in 25 ml of water, the solution filtered and rendered alkaline with ammonia. On long standing, the N-methylnordelsine crystallized out in the form of coarse truncated tetrahedra. The yield was 0.37 g. The crystallization of the methylated base was considerably facilitated if the iodine ion was preliminarily precipitated from the solution with the aid of the calculated quantity of silver oxide.

Properties. After recrystallization from dilute alcohol, the N-methylnordelsine was in the form of the crystalline hydrate which contains 4 molecules of water.

Found %: H_2O 13.83. $C_{24}H_{39}O_7N \cdot 4H_2O$. Calculated %: H_2O 13.71.

The melting point of the base depends on the quantity of solvent of crystallization. The crystalline hydrate, with 4 molecules of water, melts at 106-108° with vigorous foaming, $[\alpha]^{22}_D + 46.9°$ (c 0.64 in ethanol). The substance, dried at 40-50° or in a vacuum desiccator over calcium chloride at room temperature, loses 3 molecules of water and then has a m.p. of 130-131°, $[\alpha]^{25}_D + 52.5°$ (c 3.00 in ethanol). The compound completely dried at 100-110° does not have a crystalline structure and melts over a wide range between 85 and 98°; $[\alpha]^{25}_D + 54.6°$ (c 3.13 in ethanol).

Found %: C 61.01, 60.93; H 8.79, 8.83; N 3.05, 3.11; OCH_3 26.39, 26.25. $C_{24}H_{39}O_7N \cdot H_2O$. Calculated %: C 61.12; H 8.76; N 2.97; $4OCH_3$ 26.33.

The hydrobromide of N-methylnordelsine was precipitated with dry ether from a solution of 70 mg of the base in 0.2 ml of methanol which had been acidified with hydrobromic acid. After recrystallization from alcohol-ether, the dried salt melted rather sharply at 199° (with decomposition).

The hydriodide of N-methylnordelsine was prepared analogously from a solution of 50 mg of the base in 0.2 ml of alcohol which was acidified with colorless hydriodic acid. The salt, after having been recrystallized and dried at 105° in a vacuum, had a m.p. of 204-205° (with decomposition).

Perchlorate of N-methylnordelsine. 60 mg of the base was dissolved in 0.2 ml of methanol, and 60 mg of magnesium perchlorate and a drop of hydrochloric acid (until the reaction was acid to Congo red) were then added. Ether was added from above. After some time, crystals of the perchlorate of N-methylnordelsine began to precipitate at the boundary of the two solvents. The salt, after having been twice recrystallized from a mixture of alcohol and ether and dried at 100°, sintered at 183° and melted at 187-188° (with decomposition).

N-Ethylnordelsine

Preparation. 0.30 g of nordelsine was dissolved in 5 ml of ethanol, stirred with 0.5 ml of ethyl iodide and heated in a sealed tube on a water bath for 2 hours. The excess of ethyl iodide and ethanol was evaporated off and the solution concentrated to small volume. Ether was added to the residue. Rapidly accelerating crystallization began at once. The salt which precipitated was separated and dissolved in 2 ml of water. The aqueous solution was rendered alkaline with ammonia. The contents of the vessel were quickly filled compactly with fine silky threads of N-ethylnordelsine. After recrystallization from dilute alcohol, the alkylated base melted with foaming at 138-139°, $[\alpha]^{25}_D + 50.0°$ (c 0.80 in ethanol).

A mixed sample of the N-ethylnordelsine with an original sample of delsine displayed no melting point depression. When dried in a vacuum, the resynthesized base, similarly to the initial alkaloid, lost a molecule of water of crystallization and forms an amorphous substance $[\alpha]^{22}_D + 52.4°$ (c 0.91 in ethanol).

The hydrohalides of N-ethylnordelsine were prepared in exactly the same way as was indicated for delsine [12]. The hydrobromide of the resynthesized base melted at 183-184°, the hydriodide melted at 187°. Mixed samples of these salts with the salts of delsine displayed no melting point depression or depression of the decomposition temperature.

The perchlorate of the base was prepared by analogy with the perchlorate of N-methylnordelsine. It had a m.p. of 215° and was completely identical in its properties with the perchlorate of the natural delsine.*

Found %: C 61.62; H 9.01; N 2.94; OCH_3 25.25. $C_{25}H_{41}O_7N \cdot H_2O$. Calculated %: C 61.83; H 8.93; N 2.88; $4OCH_3$ 25.56.

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* In one of the preceding communications [12], the chlorate of delsine, $C_{25}H_{41}O_7N \cdot HClO_3$, which has a m.p. of 145-146°, was erroneously described as the perchlorate. It should be noted, that chloric acid in certain cases is one of the most convenient salt-forming reagents for the aconitine alkaloids and ordinarily gives anhydrous crystalline salts with well-expressed melting points.

SUMMARY

1. The conversion of delsine via the nitroso compound to the nor-base was accomplished. The alkylation of the latter with ethyl iodide gives a compound which is identical with the hydriodide of natural delsine.

2. The indicated series of conversions conclusively demonstrated the presence of an N-ethyl group in aconitine alkaloids.

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* See Consultants Bureau Translation, page 189.

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SUMMARY

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CHARACTERIZATION OF THE COMPOSITION OF THE ALKALOIDS OF DELPHINIUM ELATUM L.

V. V. Feofilaktov and L. D. Alekseeva

33 alkaloids from the genus Delphinium have been isolated and described in the literature which are close in their structure to the alkaloids isolated from plants of the genus Aconitum and constitute the single general group of aconitic alkaloids. A voluminous literature has been devoted to the investigation of the aconitic alkaloids. However, the chemical structure of these alkaloids has not been completely deciphered, which is explained by the exceptional complexity of their structure.

In the present work, we report the results of an investigation of an alkaloid which has not been previously described, which was obtained from the vegetable part of the "high larkspur" Delphinium elatum fam. Ranunculaceae, collected in the Altai Mountains in 1949 by the expedition headed by P. S. Massagetov. The entire aboveground portion of the plant, the alkaloid content of which amounted to 0.72% of the absolute dry weight, was subjected to investigation.

The total alkaloids obtained by the usual extraction of the vegetable portion with dichloroethane, were separated into 5 fractions, from which the fraction of weak bases, soluble in ether and present in comparatively maximum quantity in the alkaloid mixture, was taken for investigation. By a second conversion of the fraction into the salt and crystallization of the base from ether we succeeded in isolating a crystalline portion which, when dissolved in ethyl ether and precipitated with petroleum ether, crystallized in the form of triangular and hexagonal prisms. After 3-fold recrystallization, the base had a constant m.p. of 188-189°.

The alkaloid was quite soluble in chloroform, alcohol, ether and xylene; was insoluble in water and petroleum ether; and was optically active $[\alpha]^{17}_{D} -36.84°$ (in anhydrous alcohol) and $[\alpha]^{17}_{D} -26.32°$ (in chloroform). The following crystalline salts were prepared: the hydrochloride with a m.p. of 212-213° and the nitrate with a m.p. of 169-171°.

The empirical formula of the alkaloid – $C_{30}H_{47}O_9N$, which we called delphelatine – was established from the results of the elementary analysis of the base and its salts.

It became clear from the quantitative determination of the functional groups that 2 atoms of oxygen are found in the alkaloid in the form of hydroxy groups and 3 in the form of methoxy groups; the alkaloid is a tertiary base containing an N-alkyl (methyl?) group.

We present the partially expanded formula of the alkaloid:

$$C_{30}H_{47}O_9N \text{ or } C_{23}H_{28}O_2(NCH_3)(OCH_3)_3(OH)_2(OOCC_2H_5).$$

Delphelatine is an ester and is saponified by heating in a water-alcohol solution of alkali to give a crystalline amino alcohol which crystallized from ethanol in the form of coarse rectangular prisms, beveled at the corners, which melted at 235-237° and had the composition $C_{27}H_{43}O_8N$. The amino alcohol gives a crystalline hydrochloride $C_{27}H_{43}O_8N \cdot HCl$ with a m.p. of 222-223.5° and a nitrate $C_{27}H_{43}O_8N \cdot HNO_3$ with a m.p. of 199-200°. Determination of the functional groups in the amino alcohol showed the presence of three hydroxy groups; no methylenedihydroxy group was detected. We present the partially expanded formula of the amino alcohol:

$$C_{27}H_{43}O_8N \text{ or } C_{23}H_{28}O_2(NCH_3)(OCH_3)_3(OH)_3.$$

Rabinovich [1] studied the alkaloids of the vegetable parts of "high larkspur" simultaneously with us. It can be concluded from a comparison of the alkaloid eldeline described by the indicated author with the alkaloid delphelatine isolated by us (Table 1) that our base is not identical with eldeline, since it differs in composition, in the number of hydroxy groups and does not contain a methylenedihydroxy group, while this group is present in eldeline. In addition, when eldeline is saponified with alkali, it yields the amino alcohol eldelidine – $C_{25}H_{39}O_7N$ – and acetic acid; we obtained an amino alcohol with the composition $C_{27}H_{43}O_8N$, and an acid which is not acetic acid (Table 2).

TABLE 1

Property	Eldeline [1]		Delphelatine	
Base	M.p. 182-184°		M.p. 188-189°	
Formula of the base	$C_{27}H_{41}O_8N$		$C_{30}H_{47}O_9N$	
Percent composition:	Found:	Calculated:	Found:	Calculated:
Carbon	64.10, 63.82	63.91	63.49, 63.95, 63.68, 63.79	63.72
Hydrogen	8.12, 8.06	8.08	8.27, 8.48, 8.23, 8.37	8.32
Nitrogen	3.10, 2.78	2.76	2.59, 2.35, 2.38, 2.50, 2.47	2.48
Methoxy groups	18.27		18.24, 18.33, 18.30	
Hydroxy groups	3.55		5.64, 5.18, 5.74	
Methylenedihydroxy group	Present		Absent	
Hydrochloride of the base	M.p. 204-206° (decomp.)		M.p. 212-213° (decomp.)	
Nitrate of the base	M.p. 170-173° (decomp.)		M.p. 169-171° (decomp.)	
Percent content of nitrogen	Found:	Calculated:	Found:	Calculated:
	5.16, 5.20	4.91	4.72, 4.67	4.46

TABLE 2

Property	Eldelidine [1]		Amino alcohol, obtained by saponification of delphelatine	
Base	M.p. 226-228°		M.p. 235-237°	
Formula of the base	$C_{25}H_{39}O_7N$		$C_{27}H_{43}O_8N$	
Percent composition:	Found	Calculated:	Found:	Calculated:
Carbon	64.52, 64.39	64.52	64.07, 64.37, 64.17	63.91
Hydrogen	8.46, 8.47	8.38	8.48, 8.42, 8.36	8.08
Nitrogen	3.19, 3.24	3.01	2.79, 2.93, 2.72	2.76
Hydroxy groups	7.74		9.60, 10.25, 9.79	
Methylenedihydroxy group	Present		Absent	
Hydrochloride of the base	M.p. 216-218° (decomp.)		M.p. 222-223.5° (decomp.)	
Nitrate of the base	M.p. 186-188° (decomp.)		M.p. 199-200° (decomp.)	
Percent content of nitrogen	Found:	Calculated:	Found:	Calculated:
	5.18, 5.19	5.33	4.86, 4.66	4.89

TABLE 3

Alkaloid	Portion of the plant studied	Empirical formula	M	$[\alpha]_D$	M.p.
Delpheline [2]	Seeds	$C_{25}H_{39}O_6N$	449	−25.8° (in chloroform)	227°
Delatine [2]	Seeds	$C_{19}H_{25}O_3N \cdot H_2O$	315 + H_2O	+ 13.5° (in 0.5 N HCl)	148
Methyllycaconitine [2]	Seeds	$C_{37}H_{48}O_{10}N_2 \cdot H_2O$	680 + H_2O 698	+ 49.1° (in anhydrous alcohol)	128
Delphelatine	Vegetable material	$C_{30}H_{47}O_9N$	565	−26.32° (in chloroform)	188-189

The chemical study of the seeds of "high larkspur" was carried out by the English investigator Goodson in 1943 [2]. The alkaloids described by him are presented in Table 3, in which the constants of the base isolated by us — delphelatine — are also given for comparison.

As a result of the comparison of the properties of the alkaloids described by Rabinovich and Goodson, and also of all the alkaloids from plants of this genus which have been described, it can be stated that the alkaloid isolated by us is distinct from the previously known alkaloids.

EXPERIMENTAL

The vegetable material (grass) in a quantity of 9.0 kg was moistened with 10% ammonia solution and the alkaloids were extracted with dichloroethane. The dichloroethane extract was treated in its turn with 10% sulfuric acid until the alkaloids were completely extracted. The combined sulfuric acid extracts were filtered, rendered alkaline with ammonia, and the alkaloids extracted with chloroform. The alkaloids were then extracted from the chloroform with a 10% solution of hydrochloric acid. The hydrochloric acid solution obtained of the alkaloids was separated into 5 fractions in the following manner.

7.64 g of a fraction (I) of the hydrochlorides of the alkaloids which were soluble in chloroform was obtained by extracting the hydrochloric acid solution with chloroform.

After the aqueous hydrochloric acid solution had been extracted with chloroform, it was rendered alkaline with $NaHCO_3$ and extracted initially with ether and then with chloroform. Two more alkaloid fractions were obtained: 25.0 g of weak bases, soluble in ether (II), and 20.58 g of weak bases, soluble in chloroform (III).

After the mother liquor had been rendered alkaline with ammonia, the portion of strong bases remaining was extracted again, initially with ether, and then with chloroform. 2.0 g of bases which were soluble in ether (IV) and 1.96 g of bases which were soluble in chloroform (V) were obtained.

The weakly basic fraction of alkaloids (II) constituted the greater portion of the alkaloid mixture. It was the first taken for investigation.

Isolation of the Base Delphelatine

The weak base fraction (II) was dissolved in 5% sulfuric acid and after the solution had been rendered alkaline with a 25% ammonia solution, it was extracted with ether. The ethereal extracts were combined and carefully dried with roasted potash. Upon condensation of the ethereal solution, crystals were formed which had the form of triangular and hexagonal prisms. After 3-fold crystallization by dissolving it in ethyl ether and precipitation with petroleum ether, the substance was colorless and had a constant m.p. of 188-189°. The alkaloid was quite soluble in chloroform, alcohol, ether and xylene; it was insoluble in water and petroleum ether.

To demonstrate the homogeneity of the alkaloid obtained, it was dissolved in 5% H_2SO_4 and, during divided addition of alkali, was extracted with ether. Several fractions were thus obtained, the hydrochlorides of which had the same melting point.

1st fraction: hydrochloride m.p. 212-213°; 2nd fraction: hydrochloride m.p. 211-212°.

On the basis of the results of the elementary analysis, the formula $C_{30}H_{47}O_9N$ must be ascribed to the base being investigated.

8.817 mg sub.; 20.514 mg CO_2; 6.522 mg H_2O. 8.088 mg sub.: 18.955 mg CO_2; 6.134 mg H_2O. 5.017 mg sub.: 11.707 mg CO_2; 3.693 mg H_2O. 5.248 mg sub.: 12.268 mg CO_2; 3.929 mg H_2O. 17.032 mg sub.: 3.16 ml 0.01 N HCl (Kjeldahl). 17.157 mg sub.: 2.88 ml 0.01 N HCl. 14.632 mg sub.: 2.49 ml 0.01 N HCl. 7.944 mg sub.: 1.42 ml 0.01 N HCl. 8.662 mg sub.: 1.53 ml 0.01 N HCl. Found %: C 63.49, 63.95, 63.68, 63.79; H 8.27, 8.48, 8.23, 8.37; N 2.59, 2.35, 2.38, 2.50, 2.47. $C_{30}H_{47}O_9N$. Calculated %: C 63.72; H 8.32; N 2.48.

Determination of the molecular weight (of an equivalent) of the alkaloid by titration. By dissolving the alkaloid in excess 0.1 N H_2SO_4 solution and back titration with 0.1 N NaOH solution in the presence of the indicator methyl red, the following data were found:

0.1230 g sub.: 2.44 ml 0.1 N H_2SO_4. 0.1272 g sub.: 2.46 ml 0.1 N H_2SO_4. 0.1670 g sub.: 3.15 ml 0.1 N H_2SO_4. 0.1348 g sub.: 2.44 ml 0.1 N H_2SO_4. Found equiv.: 504, 517, 530, 552. $C_{30}H_{47}O_9N$. Calculated equiv.: 565.

Determination of the specific rotation:

0.2000 g substance in 10 ml alcohol (c 2.000, l 0.95 dm) α −0.7°; $[\alpha]_D^{17}$ −36.84° (in anhydrous alcohol).
0.2000 g substance in 10 ml chloroform (c 2.000, l 0.95 dm) α −0.5°; $[\alpha]_D^{17}$ −26.32° (in chloroform).

Determination of the hydroxy groups (by Tserevitinov's method):

8.760 mg sub.: 0.72 ml CH_4 (26°, 748.6 mm). 8.078 mg sub.: 0.61 ml CH_4 (26°, 748.6 mm). 9.175 mg sub.: 0.77 ml CH_4 (22°, 746.6 mm). Found %: OH 5.64, 5.18, 5.74. $C_{30}H_{45}O_7N(OH)_2$. Calculated %: OH 6.00.

Determination of the methoxy groups (by the method of Fibek and Brekher):

7.859 mg sub.: 13.88 ml 0.02 N $Na_2S_2O_3$. 8.124 mg sub.: 14.40 ml 0.2 N $Na_2S_2O_3$. 9.005 mg sub.: 15.94 ml 0.02 N $Na_2S_2O_3$. Found %: OCH_3 18.24, 18.33, 18.30. $C_{27}H_{38}O_6N(OCH_3)_3$. Calculated %: $(OCH_3)_3$ 16.46.

Determination of the alkyl group bound to the nitrogen:

7.696 mg sub.: 2.83 ml 0.02 N $Na_2S_2O_3$. 7.559 mg sub.: 3.03 ml 0.02 N $Na_2S_2O_3$. 7.945 mg sub.: 2.73 ml 0.02 N $Na_2S_2O_3$. Found %: CH_3 1.84, 2.00, 1.72. $C_{29}H_{44}O_9NCH_3$. Calculated CH_3 2.65.

Delphelatine Hydrochloride

Dry gaseous hydrogen chloride was passed into the ethereal solution of the alkaloid. The amorphous precipitate at once obtained gradually became crystalline.

The hydrochloride crystallized in the form of needles, had a m.p. of 212-213° and the composition $C_{30}H_{47}O_9N \cdot HCl$.

9.206 mg sub.: 1.42 ml 0.01 N HCl, (Kjeldahl). 8.369 mg sub.: 1.30 ml 0.01 N HCl. Found %: N 2.15, 2.17. $C_{40}H_{47}O_9N \cdot HCl$. Calculated %: N 2.32.

Delphelatine Nitrate

To a saturated solution of the base in anhydrous ether (preliminarily dried with metallic sodium and redistilled) concentrated nitric acid was added in drops (while the solution was being cooled with ice) until the reaction was weakly acid. A fine crystalline precipitate gradually settled out (tetrahedral crystal type). The precipitate was filtered off, carefully washed with ethyl ether and dried. The nitrate had a m.p. of 169-171° and the formula $C_{30}H_{47}O_9N \cdot HNO_3$.

8.212 mg sub.: 17.014 mg CO_2; 5.635 mg H_2O. 8.543 mg sub.: 17.735 mg CO_2; 5.911 mg H_2O. 7.977 mg sub.: 2.69 ml 0.01 N HCL (Kjeldahl). 7.700 mg sub.: 2.57 ml 0.01 N HCl. Found %: C 56.54, 56.65; H 7.67, 7.74; N 4.72, 4.67. $C_{30}H_{47}O_9N \cdot HNO_3$. Calculated %: C 57.32; H 7.64; N 4.46.

Thus, the data of the elementary analysis of the base, the complete analysis of the nitrate and hydrochloride of the base and the determination of the equivalent by titration lead to the same empirical formula $C_{30}H_{47}O_9N$.

Saponification of Delphelatine

1.4544 g of the alkaloid was dissolved in 7.5 ml of alcohol and 6.0 ml of 1 N NaOH was added to the solution; the reaction mixture was heated on a water bath for 3 hours, after which it was concentrated almost to dryness. The crystalline residue obtained was transferred to a filter, carefully washed with water and dried in a vacuum desiccator.

The amino alcohol was recrystallized from alcohol; the crystals had the form of rectangular prisms, beveled at the corners, a m.p. of 235-237° and the formula $C_{27}H_{43}O_8N$. The amino alcohol was quite soluble in chloroform and ether, was more difficultly soluble in alcohol and was insoluble in water.

7.606 mg sub.: 17.887 mg CO_2; 5.730 mg H_2O. 4.647 mg sub.: 10.962 mg CO_2; 3.473 mg H_2O. 5.299 mg sub.: 12.442 mg CO_2; 4.018 mg H_2O. 8.738 mg sub.: 1.70 ml 0.01 N HCl (Kjeldahl). 8.774 mg sub.: 1.82 ml 0.01 N HCl. 9.238 mg sub.: 1.82 ml 0.01 N HCl. Found %: C 64.17, 64.37, 64.07; H 8.42, 8.36, 8.48; N 2.72, 2.93, 2.78. $C_{27}H_{43}O_8N$. Calculated %: C 63.91; H 8.08; N 2.76.

Determination of the molecular weight (of an equivalent) of the amino alcohol by titration. By dissolving the base in excess 0.01 N HCl solution and back titration with 0.01 N NaOH solution in the presence of the indicator methyl red, the following data were found:

8.905 mg sub.: 2.12 ml 0.01 N HCl. 8.759 mg sub.: 1.98 ml 0.01 N HCl. 8.185 mg sub.: 1.86 ml 0.01 N HCl. Found equiv.: 420, 442, 440. $C_{27}H_{43}O_8N$. Calculated equiv.: 509.

Determination of the hydroxy groups in the amino alcohol (by Tserevitinov's method):

5.933 mg sub.: 0.87 ml CH_4 (22°, 752.2 mm). 5.571 mg sub.: 0.78 ml CH_4 (22°, 752.2 mm). 5.881 mg sub.: 0.80 ml CH_4 (19°, 752.3 mm). Found %: OH 10.25, 9.79, 9.60. $C_{27}H_{40}O_5N(OH)_3$. Calculated %: $(OH)_3$ 10.02.

Determination of the methylenedihydroxy group: 0.02 g of the alkaloid was dissolved by heating in 5 ml of phloroglucinol sulfuric acid (in a test tube).* 2 ml of concentrated sulfuric acid was added to the hot solution; the solution was stirred and heated on a boiling water bath for half an hour. The appearance of a red coloration and a flocculent precipitate was not observed, which indicates the absence of the methylenedihydroxy group.

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* The phloroglucinol sulfuric acid was prepared by dissolving 1.5 g of phloroglucinol in a mixture of 75 g of water and 50 g of concentrated sulfuric acid by heating; the solution was then cooled and, after standing for many hours, was filtered.

Hydrochloride of the Amino Alcohol

Upon passing dry gaseous hydrogen chloride into an anhydrous ether solution of the amino alcohol, needle-like crystals of the hydrochloride of the amino alcohol precipitated, which were separated, carefully washed with ether and dried in a vacuum desiccator; the m.p. was 222-223.5° (with decomposition).

7.571 mg sub.: 1.32 ml 0.01 N HCl (Kjeldahl). 8.776 mg sub.: 1.60 ml 0.01 N HCl. Found %: N 2.44, 2.55. $C_{27}H_{43}O_8N \cdot HCl$. Calculated %: N 2.56.

Nitrate of the Amino Alcohol

To a saturated solution of the amino alcohol in anhydrous ether, concentrated nitric acid was added in drops until the reaction was weakly acid; an amorphous precipitate of the nitrate of the amino alcohol settled out, which crystallized on standing. The precipitate was filtered off, carefully washed with ethyl ether and dried. After drying in a vacuum desiccator, the nitrate melted at 199-200° (with decomposition).

4.757 mg sub.: 9.766 mg CO_2; 3.211 mg H_2O. 4.505 mg sub.: 9.282 mg CO_2; 3.038 mg H_2O. 8.667 mg sub.: 2.88 ml 0.01 N HCl (Kjeldahl). 6.305 mg sub.: 2.19 ml 0.01 N HCl. Found %: C 56.02, 56.22; H 7.55, 7.54; N 4.66, 4.86. $C_{27}H_{43}O_8N \cdot HNO_3$. Calculated %: C 56.64; H 7.69; N 4.89.

SUMMARY

1. The alkaloid delphelatine – $C_{30}H_{47}O_9N$ with a m.p. of 188-189° – was isolated from the vegetable material of "high larkspur" (*Delphinium elatum*) and characterized.

2. Its crystalline salts – the hydrochloride, $C_{30}H_{47}O_9N \cdot HCl$ with a m.p. of 212-213°, and the nitrate $C_{30}H_{47}O_9N \cdot HNO_3$ with a m.p. of 169-171° – were prepared.

3. The presence in the alkaloid of two hydroxy, three methoxy, and the N-alkyl groups was established.

4. The amino alcohol $C_{27}H_{43}O_8N$, with a m.p. of 235-237° was prepared by the saponification of delphelatine.

5. The crystalline salts of the amino alcohol – the hydrochloride, $C_{27}H_{43}O_8N \cdot HCl$ with a m.p. of 222-223.5°, and the nitrate $C_{27}H_{43}O_8N \cdot HNO_3$, with a m.p. of 199-200° – were prepared.

6. The partially expanded formula of delphelatine is as follows:

$$C_{23}H_{28}O_2(NCH_3)(OCH_3)_3(OH)_2(OOCC_2H_5).$$

7. The partially expanded formula of the amino alcohol of delphelatine is as follows:

$$C_{23}H_{28}O_2(NCH_3)(OCH_3)_3(OH)_3.$$

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* See Consultants Bureau Translation, page 1743.

ON THE CORRELATION BETWEEN THE HEAT OF FORMATION OF CHEMICAL COMPOUNDS AND THE POSITION OF THE ELEMENTS IN THE D. I. MENDELEEV PERIODIC TABLE

V. P. Shishokin

Laury showed in 1882 that the quantity of heat which is evolved during the formation of chlorides, bromides and iodides of metals, is periodically dependent on the magnitude of the atomic weight of the elements. In 1892 Richards came to the conclusion that the heat of formation of metal fluorides is also found in periodic dependence on the atomic weight of the combined elements. In all these cases it turned out that the greatest quantity of heat is evolved by the alkaline metals. Mendeleev [1] noted that the heat of formation of oxides (according to the data of Thomsen) also conforms to a periodic dependence, the greatest magnitude however, occurs at the metals of the second group (magnesium, calcium, strontium and barium).

Thomsen himself indicated a periodic change of affinity toward oxygen in the groups of the Mendeleev table; thus, with chlorine and iodine, sulfur and tellurium, phosphorus and antimony a greater affinity toward oxygen is observed than respectively with bromine, selenium and arsenic. Biron [2] considered a detailed change in the properties of elements and their compounds, in particular – the heat of formation of compounds in the vertical direction in the Mendeleev table. It turned out that a number of properties and specifically the heat of formation of oxides changes periodically in the groups of the Mendeleev table; this phenomenon was designated by Biron as "secondary periodicity". Roth [3] in further experimental investigations confirmed the phenomenon of secondary periodicity in the change of the heat of formation of elements in the principal subgroups of the IV – VII groups; thus, the greatest heat of formation is observed in the elements of the odd periods while the least was observed in the elements of the even periods.

The work of Biron went unnoted both by Russian and by foreign investigators. Thus, A. M. Berkengeim [4,5] in his work on the connection of the heats of formation of chemical compounds with the position of the elements in the Mendeleev table did not take account of the phenomenon of secondary periodicity, which explains deviation of his calculated values from the experimental data. There was no reference to the work of Biron and Roth. Nothing is said concerning secondary periodicity in chemistry textbooks. Mendeleev himself [6] wrote in "Fundamentals of Chemistry": ...The affinity of iodine toward oxygen is much greater than that of chlorine. Bromine occupies an intermediate position".

Shchukarev and Vasilkova and Shchukarev, Ariya and Lakhtin [7, 8] showed the periodic change in the heat of formation of chemical compounds of magnesium with elements of the principal subgroups of groups IV and V of the Mendeleev table.

Kapustinsky did not take into account the phenomenon of secondary periodicity and came to an incorrect conclusion in his works on the establishment of a dependence between the heat of formation of chemical compounds and the position of elements in the Mendeleev table [9, 10].

Kapustinsky establishes the rule of "thermochemical logarithmicity", in accord with which a rectilinear relationship between the heat of formation of chemical compounds and the logarithm of the atomic number of the elements both in the periods and in the groups of the Mendeleev table should occur. However, while periodic change of the heats of formation of chemical compounds is present in the groups, the existence of themochemical logarithmicity can not be mathematically substantiated here.

In his theoretical basis for "thermochemical logarithmicity" Kapustinsky used the representation of Yum-Rozeri concerning the reversible proportionality between the atomic radius and the cubic root of the atomic number which can not occur while there is present a graduated change in the dimensions of the atoms in the groups [11].

The straight lines presented by Kapustinsky for the dependence between the heat of formation of radicals and oxides of the elements of the principal subgroups I and II have a very small angle of inclination as a consequence of which there occured an apparent rectification of the periodicity. In Fig. 1 the change in the heat of formation E of the chlorides of the alkaline metals is shown as a function of the changes in the logarithm of the atomic number log z of the alkaline metals on the scale of Kapustinsky (1. (figures to the right of the vertical axis), and in a greater vertical scale (2, figures to the left of the axis). The stepwise character of the line in the second case is evidence of the manifestation of periodicity; a similar picture is observed when other examples of dependence between the heat of formation of compounds and the logarithm of the atomic number are depicted in a greater vertical scale.

For the chlorides of elements of groups III and IV and chlorides of the 2-nd, 3-rd, 4-th, and 5-th periods Kapustinsky also gave "thermochemical logarithmicities"; these straight lines were constructed on a sufficiently great scale of the heats of formation of the compounds, however the observable scattering of points is undoubtedly evidence of the presence here also of periodic change. The only verifiable example of the rule of "thermochemical logarithmicity" appears to be the rectilinear dependence existing between the logarithm of the atomic number and the heat of formation of chlorides of elements of the third period.

Kapustinsky noted that the rule of "thermochemical logarithmicity" was not applicable to the gaseous state of a substance.

In the present work an attempt is made to relate the heat of formation of chemical compounds (halides and oxides of metals) with the ionization potentials of the participating elements. Just as in the works of A. M. Berkengeim and A. F. Kapustinsky, the heat effects were taken to refer to a gram equivalent. The magnitudes of the heat effects and ionization potentials were taken from the handbook of Kei and Lebi [12].

The periodicity of the changes in the heats of formation of halides and oxides of metals in groups of the Mendeleev table is not clearly manifested. However the presence of periodicity can be shown in the change of heat effects using the processes employed by Rydberg and Bazarov to display the periodicity of the changes in the atomic weight of elements; according to the Rydberg method [1] the differences of two series of stationary quantities are compared, while according to the Bazarov method [13], the ratios of these quantities are compared.

In Tables 1 and 2 the ratios of the heats of formation of a number of significant solid halides of the alkaline metals are set forth; secondary periodicity is evident in all cases.

TABLE 1

LiF : NaF	1.01	LiCl : NaCl	0.99	LiBr : NaBr	0.97	LiI : NaI	0.94
NaF : KF	1.07	NaCl : KCl	0.94	NaBr : KBr	0.92	NaI : KI	0.88
KF : RbF	1.009	KCl : RbCl	0.993	KBr : RbBr	0.982	KI : RbI	0.973
RbF : CsF	1.011	RbCl : CsCl	0.989	RbBr : CsBr	0.981	RbI : CsI	0.966

TABLE 2

LiF : LiCl	1.49	NaF : NaCl	1.46	KF : KCl	1.29	RbF : RbCl	1.27	CsF : CsCl	1.24
LiCl : LiBr	1.16	NaCl : NaBr	1.13	KCl : KBr	1.11	RbCl : RbBr	1.09	CsCl : CsBr	1.09
LiBr : LiI	1.29	NaBr : NaI	1.25	KBr : KI	1.19	RbBr : RbI	1.18	CsBr : CsI	1.17

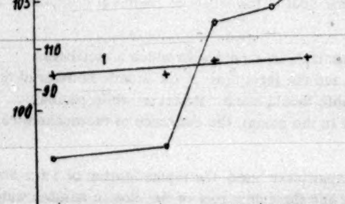

Fig. 1. Dependence between the heat of formation E of chlorides of the alkaline metals and the atomic number of the metal log z. 1) On the scale of A. F. Kapustinsky; 2) at a greater vertical scale.

Fig. 2 shows that the heat of formation of the halides of the alkaline metals is linearly dependent on the square root of the magnitude of the first ionization potential of the metal; the angle of inclination of the straight lines changes stepwise in proceeding from iodides to fluorides. If with the iodides, bromides and chlorides of the alkaline metals the heats of formation are associated with a reversible dependence on the ionization potentials of the metal, with the fluorides there still occurs a straight line dependence. The greater the affinity of the halogen for electrons, the less the extent to which the ionization potential of the metal influences the heat of formation of the halide.

The heat of formation of NaF of 136 keal (Fig. 2) set forth in the handbooks considerably deviates from the straight line for fluorides; interpolation gives a heat of formation of NaF of 142 kcal (according to Kapustinsky, 144 kcal).

Inasmuch as both the ionization potential and the heat of formation change periodically in the groups, the existence of a rectilinear dependence between the heats of formation and the ionization potentials is possible only under definite physico-mathematical conditions.

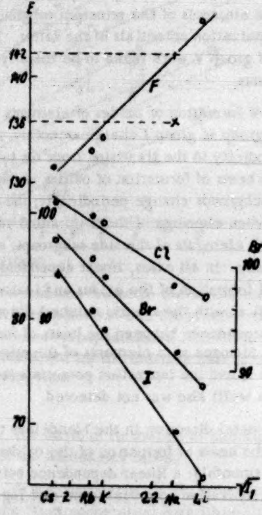

Fig. 2. Dependence between the heat of formation E of alkaline metal halides and the square root of the first ionization potential of the metal. The scale for iodides and fluorides is on the left of the axis; that for chlorides is on the right.

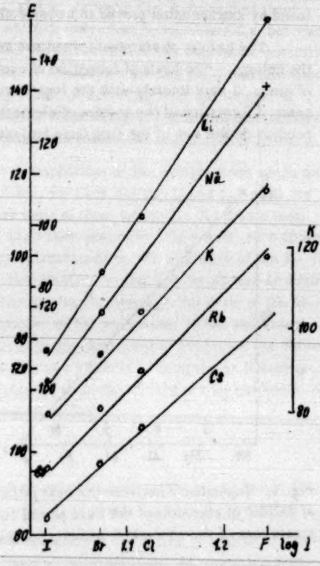

Fig. 3. Dependence between the heat of formation E of halides of the alkaline metals and the logarithm of the first ionization potential of the halogen. The scales for the halides of Cs and Na are to the left of the axis; those for the halides of Rb and Li are to the right.

It was natural to expect further that the heats of formation of the halides of the alkaline metals would be found in some dependence on the magnitudes of the affinity for electrons (null ionization potential) of the halogen. However, to demonstrate such a dependence, expressible by a simple method, was not successfully done, and it turned out that the heats of formation of the halides of the alkaline metals is associated with a rather good linear dependence on the logarithm of the first ionization potential of the halogen (Fig. 3). It is possible that errors in the determination of the electron affinity were too great (particularly with fluorine), and the first ionization potential, in general determinable with greater accuracy, can replace the null potential (the magnitudes of the latter are taken from the book of Syrkin and Dyatkina [14]).

It should be assumed in general that the heat of formation of the halide is increased with increase in the electron affinity of the halogen. The heat of formation of NaF (142 kcal) obtained by interpolation in Fig. 2, lies on the straight line for sodium (Fig. 3).

The simplest dependence between the heats of formation of the solid halides of the elements of the principal subgroup of group II and the ionization potentials of the latter turned out to be somewhat different. Specifically, these heats vary linearly with the square of the group ionization potential (the total of the first two potentials) of the metal; the heat of formation of the given halides is associated) semi logarithmically, with the first potential as occurred in the preceding case.

While the heats of formation of the chlorides, bromides and iodides of the metals of the principal subgroup of group II increases smoothly with increase in the atomic number (and correspondingly with decrease in the ionization potentials), the heats of formation of the fluorides exhibited a marked scattering of the points plotted from the available data; in addition, the heat of formation of BeF_2 is completely absent. All this forced us to question the correctness of the heats of formation of fluorides indicated in the literature. Only the heat of formation of BaF_2 also fits precisely on the straight line relating the heats of formation of the metals of the principal subgroup of group II to the logarithm of the first ionization potential; the points for SrF_2, CaF_2 and MgF_2 lie considerably above the corresponding curves. The heats of formation of SrF_2, CaF_2, MgF_2 and also of BeF_2 found by extrapolation proved to be respectively equal to 282, 273, 240 and 203 kcal.

The halides of aluminum, lead and antimony proved to vary linearly with the first ionization potential of the halogen. The heats of formation of compounds of aluminum with the elements of the principal subgroup of group VI vary linearly with the logarithm of the sum of the first two ionization potentials of the latter. The heats of formation of the iodides of elements of the principal subgroup of group V were found to be linearly dependent on the sum of the first three ionization potentials of these elements.

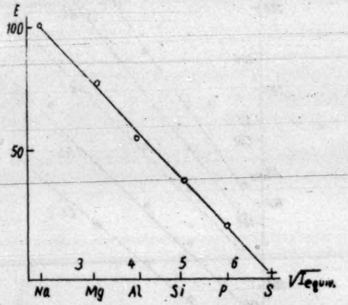

Fig. 4. Dependence between the heat of formation E of halides of elements of the third period and the square root of the equivalent potential of the element.

The heats of formation of oxides of elements of the principal subgroup of group I change smoothly; in group II there is a periodicity in the transition from Ca to Ba. In groups III – V the heats of formation of oxides of the elements of the principal subgroups change periodically; the periodicity is observed also when elements of the 2-nd and 3-rd periods are combined with elements of the side subgroups, as was done by Kapustinsky. In all cases, linear dependence between the heats of formation of the oxides and ionization potentials (as well as with the atomic number) did not appear. Linear dependence between the heats of formation of compounds of nitrogen with elements of the principal subgroup of group II and the ionization potentials (and the atomic number as well) also was not detected.

In the horizontal direction in the Mendeleev table (in the periods) the heats of formation of the oxides of the elements change smoothly; a linear dependence between the heats and the ionization potentials (and also log z) is absent.

The heats of formation of chlorides in the 2-nd, 4-th and 5-th periods change periodically; there is no linear dependence between the heats and the ionization potentials (and also log z). Only in the 3-rd period where the heats of formation of the chlorides change smoothly, does a linear dependence (Fig. 5) between them and the square root of the equivalent potential) occur (this term is used to designate the quotient resulting from the division of the group potential by the group number).

In exactly the same way a linear dependence between the heats of formation and log z is observed for the chlorides of the elements of the 3-rd period. The heat of formation of SCl_6 determined from Fig. 4 by extrapolation amounts to 3 kcal. per 1 equiv. or 18 kcal. per 1 g-formula (Kapustinsky gives 40 kcal). In general, the heats of formation of chlorides in the periods of the Mendeleev table is associated with a reversible dependence on the equivalent potentials of the elements.

In the case of gaseous molecules there occurs a clear periodicity in the change in the heats of formation of the fluorides and partially of the chlorides of the alkaline metals; with Bazarov's method it is also manifested with the remaining halides of these metals. The iodides, bromides and chlorides exhibited the existence of a rectilinear dependence between the heats of formation and the square root of the first ionization potential of the alkaline metal, the fluorides (in particular, KF) give a certain deviation from rectilinear dependence. The linear dependence between the heats of formation of the gaseous halides of the alkaline metals and the electron affinity is also not shown, as in the case of the solid halides. Correspondingly a rectilinear dependence is apparent between the heats of formation and the logarithm of the first ionization potential.

The heats of formation of gaseous molecules of the halides of hydrogen also vary linearly with the logarithm of the first ionization potential of the halogen. Thus, in contrast to the conclusion of Kapustinsky the simplest law is observable during the formation of gaseous molecules.

The presence of a linear dependence for the chlorides of the elements of the 3-rd period between the heats of their formation, on the one hand and the square root of $I_{equiv.}$ and log z on the other hand, still does not in itself influence the existence of a simple dependence between the equivalent potential and the atomic number. For chlorides of elements of the 2-nd, 4-th and 5-th periods a dependence between the heats of formation, on the one hand, and the square root of $I_{equiv.}$ and log z, on the other hand, is expressed by equidistant curves which also should argue in favor of the presence of the simplest dependence between $I_{equiv.}$ and z. Actually Fig. 5 shows that there exists a dependence which is very close to rectilinearity, between the atomic number and the square root of the equivalent potential (analogously to the law of Moseley); the scale for the square root of $I_{equiv.}$ is a sliding scale. It is evident that the tangent of the angle of inclination of these straight lines varies periodically in the series of the Mendeleev table.

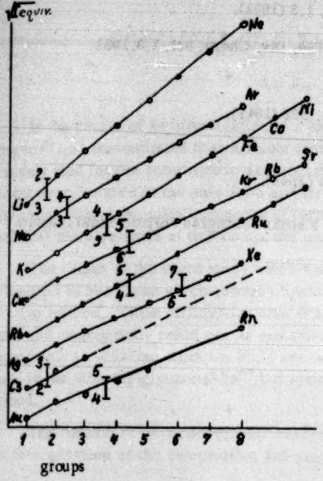

Fig. 5. Dependence between the square root of the equivalent potential and the atomic number of the element (group number)

The scale for the ordinate axis is given on the lines.

It was found by extrapolation of the straight lines which express Moseley's law that I_9 for Co is 202 and I_9 and I_{10} for Ni are 209 and 245, and on the basis of these quantities the square roots of the corresponding equivalent potentials (Co = 9.55, Ni = 10.4); were calculated; these quantities fit on the extension of the K – Fe straight line. The points obtained in this way for Rb and Sr deviate somewhat from the Rb – Ru straight line. On the basis of the Rb – Ru straight line the magnitude of the square root of the equivalent potential of niobium (5.19) was determined, and hence the value of I_1 for this element (6.4 eV) which is lacking in the literature; the first ionization potential of niobium obtained by extrapolation by Moseley's law amounts to 6eV.

SUMMARY

1. The heats of formation of chemical compounds vary in general periodically both in the groups and in the periods of the Mendeleev table.

2. As a consequence of the presence of periodicity in the change of the heats of formation of chemical compounds the "thermochemical logarithmicity" of Kapustinsky can not be theoretically substantiated and is not practically confirmed.

3. There exists a dependence between the heats of formation of chemical compounds and the ionization potentials of the elements; the heats of formation vary inversely in dependence on the ionization potentials of the cation (oxidant) and in direct dependence on the ionization potentials of the anion (reductant). In many cases this dependence can be expressed by the simplest (linear) method. The linear dependence has a somewhat different form for various groups of compounds which is apparently due to difference in the nature of the bond in the compounds. The regularities displayed are applicable both for the gaseous and for the solid state of a substance; they permit the calculation of the heats of formation of chemical compounds which have not been determined by experimental means and the introduction of corrections in a number of the available data.

4. There exists a linear (or close to linear) dependence between the atomic number and the square root of the equivalent ionization potential of the elements.

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* See Consultants Bureau Translation. p. 929.

COMPLEXES OF DIVALENT IRON WITH DIMETHYLGLYOXIME

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In the course of an investigation of a number of complex compounds of dimethylglyoxime with metals Chugaev [1,2] demonstrated that divalent iron in an alkaline medium forms a red colored compound. This reaction is widely used for the colorimetric determination of ferrous iron. However up to the present time the compound has not been isolated in the pure form and its composition has not been established. Chugaev and Orelkin [3] succeeded only in isolating a complex compound of ferrous iron with dimethyl glyoxime and pyridine $Fe(HDm)_2.2Py$; any physico-chemical characteristics of this compound were entirely lacking.

The causes of the slight study which has been devoted to this compound are associated with the experimental difficulties to overcome which proved impossible during the investigation of the complexes by the classical preparative method. These difficulties were due above all to the fact that dioxime of iron (II) is quite soluble in water and consequently could not be successfully isolated by crystallization. Further, the complex under study is formed only in alkaline medium while under these conditions ferrous iron is very rapidly oxidized in air. In addition, in the dimethylglyoxime-Fe^{++} ion system, apparently, not one, but several varied compounds (see below) are formed.

The method of physicochemical analysis of solutions of complex compounds was used in the present work for the determination of the composition and properties of the dioxime complex of divalent iron.

EXPERIMENTAL

1. Determination of the Composition of the Complex by the Isomolar Series Method. The principle of the method of determining the composition of complexes in solution according to Ostromyslensky [4] and Job [5] is based, as is well known, on the study of the optical density of series of solutions containing the reaction components in various ratios with the sum of their molar concentrations constant. The measurements of the optical density were carried out on an FM optical photometer.

Preliminary experiments established that in the presence of ammonia a compound is formed with a light absorption maximum close to 530 mμ. Upon substituting pyridine for ammonia the absorption spectrum is displaced toward the short wave portion and the light absorption maximum is observed close to 496 mμ.

For the study of the colored complex of ferrous dioxime, the initial solutions of $FeSO_4 \cdot (NH_4)SO_4 \cdot 7H_2O$ (0.01 mole/liter) and an alcoholic solution of dimethyl glyoxime (0.01 mole per liter) were prepared. These solutions were mixed in various ratios, with their total volumes always amounting to 10 ml. To diminish the oxidation of ferrous iron, hydrazine sulfate was introduced and to prevent the precipitation of the hydrate of ferrous or ferric oxide tartaric acid was added. To prepare the solutions we used the method recommended for the colorimetric determination of ferrous iron. To x ml of 0.01 molar solution of Mohr's salt 8 ml of a saturated solution of hydrazine sulfate, 0.5 ml of 5% tartaric acid solutions and $(10 - x)$ ml of 0.01 molar alcoholic solution of dimethylglyoxime was added. The solution was heated, 5 ml of 25% ammonia was added, boiled for 30 seconds, cooled under a faucet to 19° and diluted to 25 ml with a mixture of solutions of ammonia and hydrazine (in a ratio of 1:1) or of water. Then the optical density of each of the solutions at a layer thickness of 1 mm, using the light filter indicated above, was measured.

The dependence of the optical density on the ratio of the reacting components is shown in Fig. 1. On the abscissa are plotted the quantities of ferrous iron and dimethylglyoxime in milliliters and on the ordinate – the optical density of the solutions. As is evident from the figure, the maximum light absorption of the complex is observed under the given conditions at a ratio of iron to dimethylglyoxime equal to 1:2.

2. Determination of the Composition of the Complex at Constant Concentration of One of the Components and Variable Concentration of the Other. Under the conditions of the physico-chemical analysis the series of isomolar solutions is one of the sections of the diagram of the system: central ion–coordinated ion–solvent [6]. When the complex is slightly dissociated, its composition can also be determined by other sections of the system. In particular, the sections have great significance which correspond to the following series of solutions: a) constant concentration of the central ion and variable concentration of the reagent containing the coordinated ion; b) constant concentration of the coordinated ion and variable concentration of the central ion.

These experiments are also important in order to explain whether or not one compound or several compounds of varying composition are formed in the given concentration limits. Finally, these experiments are necessary for further investigation of the physico-chemical constants of the complex.

The compositions of all three sections can coincide only if under the given conditions the complex is rather stable, particularly, in relation to the presence of substances like reductants (hydrazine) and which form collateral complexes (tartaric acid). The rather sharp maximum of the curve in Fig. 1 shows that, apparently, the complex is slightly dissociated and weakly decomposed by the collateral substances which are present.

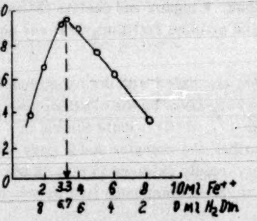

Fig. 1. Dependence of the optical density : D on the ratio of divalent iron to dimethylglyoxime.

Separate experiments set up to study the behavior of the complex on dilution showed that in dilute solutions of the complex with a concentration of Fe^{++} of $5 \cdot 10^{-4}$ mole in a 16-fold solution of ammonia and with addition of hydrazine an appreciable increase in the dissociation is not observed, since the total optical density (with observations from above, i.e. in the entire thickness of the layer) is not diminished.

The results of the measurements are shown for a series of type (a) on Fig. 2, and for a series of type (b) on Fig. 3. In solutions of series (b) the concentration of dimethyl glyoxime was $8 \cdot 10^{-4}$ mole while the concentration of ferrous iron was changed from $1 \cdot 10^{-4}$ to $12 \cdot 10^{-4}$ mole. In series (a) the concentration of Fe^{++} was $4 \cdot 10^{-4}$ while the concentration of dimethylglyoxime was changed from $2 \cdot 10^{-4}$ to $20 \cdot 10^{-4}$ mole. As is evident from Figs. 2 and 3, the curves indicate a rather sharp break at a ratio of ferrous iron and dimethylglyoxime close to 1:2.

Finally, it is evident from the conditions of preparation of the solutions and the data of Figs. 2 and 3 that at complete association of one of the components (i.e., with excess of the other component) the following is observed. An approximately identical optical density is obtained at a concentration $[Fe^{++}] = 4 \cdot 10^{-4}$ mole (with excess dimethylglyoxime) and, on the other hand, at a concentration $[H_2Dm] = 8 \cdot 10^{-4}$ mole (at an excess of iron).

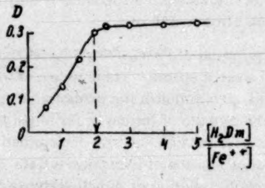

Fig. 2. Dependence of the optical density D on the dilution.

Explanation in the text

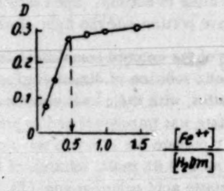

Fig. 3. Dependence of the optical density D on the dilution.

Explanation in the text.

All these data confirm that the composition of the colored complex under the given limiting conditions corresponds to a ratio of ferrous iron to dimethylglyoxime equal to 1:2. This gives a basis for considering that the composition of ferrous dioxime corresponds to the formula $Fe(HDm)_2$; thus the soluble colored complex of ferrous iron is analogous in composition to the difficultly soluble nickel compound.

3. Determination of the Dissociation Constant of the Complex. The dissociation constant of the complex characterizes its strength and is of direct significance as a basis for determining the conditions of the colorimetric determination. In addition, it was important to confirm the formula of the compound proposed above in the following respect. All the preceding experiments only make it possible to establish the ratio Fe^{++}:H_2DM. However with the same ratio the formation of an addition product of a molecule of dimethylglyoxime, for example, $[Fe(H_2Dm)_2]^{++}$ or $FeX_2 \cdot 2H_2Dm$ was possible. Further, all the curves indicated above would have the same form if the composition of the complex corresponded to the formula of the disubstituted salt, for example $FeDm_2^{--}$ (or $(NH_4)_2FeDm_2$ and others.).

The study of the dependence of the equilibrium on the concentration of H^+ ions makes it possible to answer the question raised above. If the complex has the composition $Fe(HDm)_2$, then the equilibrium should be expressed by the equation

$$Fe^{++} + 2H_2Dm = Fe(HDm)_2 + 2H^+. \tag{1}$$

The equilibrium constant should have the form:

$$K''_{\text{equil.}} = \frac{[Fe(HDm)_2][H^+]^2}{[Fe^{++}][H_2Dm]^2} \tag{2}$$

Evidently, in the case of the formation of an addition product of a dimethylglyoxime molecule, the equilibrium state should not depend at all on the pH of the solution. If a compound is formed where both hydrogen atoms of dimethylglyoxime are replaced, the equilibrium should depend on the fourth power of the change of concentration of H^+ ions, in accordance with the equation

$$Fe^{++} + 2H_2Dm = FeDm_2^{--} + 4H^+ \tag{3}$$

It is well known [8] that the first acid dissociation constant of dimethylglyoxime is equal to $8 \cdot 10^{-12}$; consequently, in a solution with a pH less than 10, dimethylglyoxime is found almost entirely in the form of the H_2Dm molecule.

In connection with what has been said a number of experiments were set up to determine the equilibrium constants at various pH values of the solution. To obtain well measurable results it was necessary to set up the experiments under conditions in which increase in the concentration of hydrogen ions caused appreciable diminution in the optical density of the solution. It was preliminarily established that this is observed at a pH of about 6.5-8. At pH approximately equal to 7 and at greater concentrations of Fe^{++} ions it is possible to partially precipitate the hydrate of ferrous oxide [7]. The use of any compound which forms a complex (as tartaric acid, etc.) is inconvenient, since in this case, evidently, the equilibrium concentration of free Fe^{++} ions will be considerably less than the total concentration of ferrous iron not bound to dimethylglyoxime. The latter circumstance does not interfere with the explanation of the question raised above concerning the composition of the dioxime; since for this purpose it was necessary to measure only the degree of displacement of the equilibrium at changing pH of the solution. However, it was impossible to set up the direct calculation from these same data of the numerical values of the instability constants of ferrous dioxime.

Experiment showed that in dilute solutions at Fe^{++} concentrations of the order of 10^{-4} - 10^{-5} mole in the presence of a sufficient excess of dimethylglyoxime, it is not necessary to introduce tartaric acid, since under these conditions a precipitate of $Fe(OH)_2$ is not formed. It is true that rather rapid oxidation in air is observed; consequently the measurement of the optical density was carried out by us as rapidly as possible after the preparation of each solution. In addition, hydrazine sulfate, the solution of which was preliminarily brought by addition of alkali to the necessary pH value, was introduced into the solution. This solution plays the role of a buffer and at the same time reduces the oxidation of ferrous iron. In order to diminish the influence of oxidation of the iron by air, it was convenient to work with as concentrated as possible solutions of the complex. In view of the intense coloration of such solutions the optical density was measured with layers of small thickness.

The solutions for measuring the optical density were prepared in the following manner. To 10 ml of previously prepared solution, containing hydrazine sulfate and alkali, 1 ml of a solution of Mohr's salt (10^{-2} mole per liter) and 1 ml of 0.1 molar alcoholic dimethylglyoxime solution were added. The optical density of the colored solution obtained was measured with a light filter with an effective wave length of 533 mμ, at a layer thickness of 1 mm. In a separate test sample, containing 10 ml of buffer solution and 1 ml of Mohr salt (i.e., without dimethylglyoxime), the pH was verified by a colorimetric method (with a two color indicator). The results of the measurements of optical density at various pH values of the solution are set forth in the table.

Taking into account the conditions of the experiments and the possible errors (in particular the partial oxidation of Fe^{++}), we utilized the following method of treating the results. At a pH approximately equal to 7.7 it can be assumed that the iron is completely bound in the colored complex; consequently the ratio of the optical density in each separate experiment (D_n) to the optical density D = 0.65 gives the ratio of the concentrations $[Fe_{\text{complex}}]$ / $[Fe_{\text{total}}]$. These data are set forth in column 3 of the table. Knowing both concentrations ($[Fe_{\text{complex}}]$ and $[Fe_{\text{total}}]$) we can calculate (by differences) the concentration of the Fe^{++} ions which are not bound in the complex and find the ratio of the concentrations of the complex-bound and unbound iron, i.e., $[Fe(HDm)_2]/[Fe^{++}]$. These ratios are set forth in column 4 in the form of their logarithms.

Expressing the constants of equation (2) logarithmically, we obtain:

$$\log K'' = 2 \log [H^+] + \log \frac{[Fe(HDm)_2]}{[Fe^{++}]} - 2 \log [H_2Dm]. \tag{4}$$

Keeping in view that in all the solutions there was a sufficient excess of free dimethylglyoxime, we can calculate the constant concentration [H_2Dm] and transform equation (4) in the following manner:

$$\log \frac{[Fe(HDm)_2]}{[Fe^{++}]} = 2pH + const. \qquad (5)$$

This relationship should be expressible by a straight line; if on the graph identical scales for log $[Fe(HDm)_2]/[Fe^{++}]$ and for pH are takem, then, evidently, the tangent of the angle of inclination of the straight line will be equal to the coefficient at the pH, i.e. must be tan $\alpha = 2$. In this case, if the reaction were proceeding in accord with equation (3), tan α would be equal to 4.

TABLE

pH	Optical density	$\frac{[Fe_{complex}]}{[Fe_{total}]}$	$\log \frac{[Fe_{bound}]}{[Fe_{free}]}$	$K'_{equil.} = \frac{[FeHDm^+][H^+]}{[Fe^{++}][H_2Dm]}$	$K''_{equil.} = \frac{[Fe(HDm)_2][H^+]^2}{[Fe^{++}][H_2Dm]^2}$
5.6	0.04	0.06	−1.19	$1.93 \cdot 10^{-5}$	$(5.85 \cdot 10^{-9})$
5.8	0.05	0.08	−1.06	$1.66 \cdot 10^{-5}$	$(3.17 \cdot 10^{-9})$
6.0	0.08	0.12	−0.86	$1.64 \cdot 10^{-5}$	$(1.98 \cdot 10^{-9})$
6.2	0.12	0.18	−0.66	$1.67 \cdot 10^{-5}$	$(1.01 \cdot 10^{-9})$
6.5	0.15	0.23	−0.52	$(1.14 \cdot 10^{-5})$	$0.43 \cdot 10^{-9}$
6.7	0.28	0.43	−0.12	$(1.81 \cdot 10^{-5})$	$0.44 \cdot 10^{-9}$
6.9	0.37	0.57	0.12	$(2.01 \cdot 10^{-5})$	$0.31 \cdot 10^{-9}$
7.1	0.50	0.77	0.52	$(3.20 \cdot 10^{-5})$	$0.31 \cdot 10^{-9}$
7.3	0.57	0.87	0.82	$(4.04 \cdot 10^{-5})$	$0.24 \cdot 10^{-9}$
7.4	0.60	0.92	1.06	$(5.52 \cdot 10^{-5})$	$0.26 \cdot 10^{-9}$
7.5	0.62	0.95	1.27	$(7.24 \cdot 10^{-5})$	$0.27 \cdot 10^{-9}$
7.7	0.65	1.00	–	–	–
7.9	0.65	1.00	–	–	–

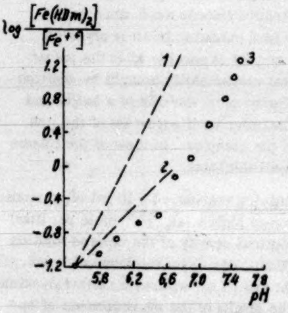

Fig. 4. Dependence of the logarithm of the ratio of the concentrations of complex bound and unbound iron on the pH.
1) Tan $\alpha = 2$; 2) tan $\alpha = 1$; 3) experimental data.

In Fig. 4 the results obtained on the basis of the experiments considered in the table are noted by the points. As is evident, the points do not fit on a single stright line, which suggests the presence in the system, in addition to $Fe(HDm)_2$, of still other complex compounds. But beginning at a pH approximately equal to 6.5 and higher the points almost fit on a straight line, the tangent of the angle of inclination of which, tan $\alpha = 2$. A dependence which corresponds to tan $\alpha = 4$ is not found in any pH range; thus, the hypothesis to the effect that the reaction at the given pH can proceed in accord with equation (3) must be rejected. In exactly the same way, evidently there is no basis for assuming the formation of a product of the addition of the dimethylglyoxime molecule. According to the data of Fig. 4 it is evident that up to pH 6.2 — 6.5 the inclination of the curve corresponds to the coefficient at H^+ equal to 1. The results of the calculations set forth in column 5 of the table, confirm these conclusions. Actually, the calculated value of the equilibrium constant $K'_{equil.} \frac{[FeHDm^+][H^+]}{[Fe^{++}][H_2Dm]}$ proves to be rather constant in the pH range from 5.6 to 6.2. After this the value of the constant begins to significantly change (the corresponding values are placed in parentheses), since the equilibrium ceases to correspond with equation (8). On the other hand, the values of the constant, calculated on the basis of equation (2) (column 6 of the table), prove to be variable at pH values from 5.6 to 6.2 (these values are placed in parentheses in the table); however at pH > 6.2 the values of $K''_{equil.}$ become constant; In connection with what has been said during the calculation of the average value $K''_{equil.}$ [in accord with equation (1)] attention is paid only to the values obtained in the pH range from 6.5 to 7.5.

$$K''_{equil.} = \frac{[Fe(HDm)_2][H^+]^2}{[Fe^{++}][H_2Dm]^2} = 0.32 \cdot 10^{-9} \qquad (6)$$

The first acid dissociation constant of dimethylglyoxime [8] is equal to $K_{H_2Dm} = \frac{[H^+][HDm^-]}{[H_2Dm]} = 8 \cdot 10^{-11}$.

Comparing the expression for the constant of equation (2) with the first acid dissociation constant of dimethylglyoxime and the instability constant of the complex $K_{complex} = \frac{[Fe^{++}][HDm^-]^2}{[Fe(HDm)_2]}$ we obtain: $K_{equil.} = \frac{K^2_{H_2Dm}}{K_{complex}}$. From this the value of the instability constant of the complex of divalent iron with dimethylglyoxime can be calculated:

$$K_{complex} = \frac{[Fe^{++}][HDm^-]^2}{[Fe(HDm)_2]} = \frac{(8 \cdot 10^{-12})^2}{0.32 \cdot 10^{-9}} = 2.0 \cdot 10^{-13}. \quad (7)$$

4. Other Complexes in the System Fe^{++} – Dimethylglyoxime in Solution. During the reaction of the central ion with the coordinated ion in solution, depending on the concentration conditions, there are ordinarily formed several complex groups of varying composition. A more detailed investigation of the system Fe^{++} – dimethylglyoxime showed that the complex $Fe(HDm)_2$ described above, although it appeared predominant over a rather wide range of concentrations, none the less is not the sole compound in this system. Omitting the experimental details, a number of data can be adduced which indicate the formation of other complex groups which differ from that described above in the ratio $Fe^{++} : H_2Dm$ and in stability.

During the study of the equilibrium formation of the complex at various pH values it could be shown (Fig. 4), that in more acidic medium (pH approximately equal to 5.4-6.5) the value of tan α is approximately equal to 1. This means that in this portion of the concentration conditions the equilibrium of the reaction between Fe^{++} and H_2Dm depends on the first power on the concentration of H^+ ions. In this range of conditions it is most probable to consider the reaction to be

$$Fe^{++} + H_2Dm = (FeHDm)^+ + H^+ \quad (8)$$

(The corresponding values of $K'_{equil.}$ are shown in column 5 of the table).

The formation of a similar complex group ($FeHDm^+$) is confirmed by a number of other data. Thus, the series of isomolar solutions at very low concentrations of the reacting components gives results which differ from the curve of Fig. 1; under these conditions displacement of the maximum in the direction of the ratio $Fe^{++}:H_2Dm = 1.1$ is observed. It is true that in strongly diluted solutions it is difficult to eliminate the influence of the oxygen of the air; consequently we carried out several additional experiments. The colored complex formed in the system $Fe-H_2Dm$ was partially extracted with several organic solvents; it was thereupon observed that, if an excess of Fe^{++} ions was introduced into the aqueous phase, then the color of the extract was appreciably different from the color of the extract obtained with excess dimethylglyoxime. Finally, during the electrolysis of an aqueous solution containing excess Fe^{++} (relative to the dimethylglyoxime), the movement of the colored layer to the cathode is observed. With excess Fe^{++}, it is evident, the following reaction occurs:

$$Fe(HDm)_2 + Fe^{++} = 2FeHDm^+. \quad (9)$$

In addition to the $FeHDm^+$ complex described above [along with $Fe(HDm)_2$], at least one additional complex is also formed in stongly alkaline medium with excess dimethylglyoxime anions. This is confirmed by the following data. As was shown above, the colored complex $Fe(HDm)_2$ is formed only at pH approximately equal to 7 while a complex analogous in composition to the difficultly soluble nickel complex is also formed in a more acid medium. This indicates that the energy of the chemical bond between Ni^{++} and HDm^- ions is considerably greater than the energy of the chemical bond between the Fe^{++} and HDm^- ions. Thus, the equilibrium

$$Fe(HDm)_2 + Ni^{++} \rightleftharpoons Ni(HDm)_2 + Fe^{++} \quad (10)$$

must be strongly displaced to the right. The constant of this equilibrium must be equal to:

$$K_{equil.} = \frac{Fe^{++}}{[Ni^{++}][Fe(HDm)_2]} = \frac{K_{complex}}{K_{s(Ni(HDm)_2)}} \quad (11)$$

The solubility product of nickel dioxime is equal to:

$$K_{s(Ni(HDm)_2)} = [Ni^{++}][HDm^-]^2 = 2 \cdot 10^{-25}.$$

Placing the value of K_s and $K_{complex}$ in equation (11), we obtain:

$$K_{equil.} = \frac{K_{complex}}{K_{s(Ni(HDm)_2)}} = \frac{2 \cdot 10^{-13}}{2 \cdot 10^{-25}} = 1 \cdot 10^{12}.$$

This quantity shows that equilibrium (10) must be almost completely displaced to the right. Actually, if nickel salt is added to a weakly alkaline solution (pH approximately equal to 8) of Fe $(HDm)_2$, a red precipitate of nickel dioxime is at once formed. This precipitate is excellently extracted by chloroform*, and the aqueous phase is completely decolorized. This confirms the conclusion set forth above. However, if a similar experiment is performed at a greater excess of NH_4OH, then the precipitate of nickel dioxime is not formed. By shaking such a solution with chloroform, absolutely no extraction of nickel dioxime is observed.

On the basis of the latter data, by analogy with other complexes of metals with weakly monobasic acids, and also by analogy with the Cu^{++} – dimethylglyoxime system [9], the formation of complexes of disubstituted salts can be assumed according to the following reaction:

$$Fe(HDm)_2 + 2OH^- = (FeDm_2^{--}) + 2H_2O$$

or

$$Fe(HDm)_2 + OH^- = FeDm + HDm^- + H_2O$$

It is well known that the precipitate of nickel dioxime is dissolved in caustic alkalis which, apparently, is associated with the formation of a similar di-substituted compound of dimethylglyoxime $NiDm_2^{--}$ [10]. However as a consequence of the very small solubility of nickel dioxime $Ni(HDm)_2$ a similar process takes place for it only with excess caustic alkali. At the same time, for the quite soluble $Fe(HDm)_2$ complex a similar process must occur considerably earlier, i.e., at a smaller excess of OH ions.

The very energetic oxidation of Fe^{++} in strongly alkaline solutions extraordinarily complicates the more exact investigation of the equilibrium and composition of the complexes being formed. None the less, the experiments set forth show the formation of ferrous dioxime to be stronger than nickel dioxime.

SUMMARY

The method of physico-chemical analysis of solutions was utilized for the study of the colored complex of the dioxime of divalent iron. The optical density was measured as a property of the system. It was found by the method of isomolar series and by other sections of the $Fe^{++} - H_2 - H_2Dm$ system that the composition of the complex at pH approximately equal to 6.5–8 corresponds to a ratio of $Fe^{++} : H_2Dm$ equal to 1:2.

The dependence of the equilibrium of the reaction on the concentration of H^+ ions was studied. On the basis of these data the instability constant of the complex was calculated:

$$K_{complex} = \frac{[Fe^{++}][HDm^-]^2}{[Fe(HDm)_2]} = \frac{(8 \cdot 10^{-12})^2}{0.32 \cdot 10^{-9}} = 2 \cdot 10^{-13}$$

It was shown that in more acid medium, and also with excess Fe^{++}, another complex group is formed; it is most probable that this is $FeHDm^+$.

In more alkaline medium with excess dimethylglyoxime anions a more stable complex is formed in which iron replaces 2 hydrogen atoms of the dimethylglyoxime.

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* Ferrous dioximin is not extracted under these conditions.

** See Consultants Bureau Translation, p. 973.

SOLUBILITY IN THE WATER–ETHYL ALCOHOL–AMMONIUM DIFLUORIDE SYSTEM AT 25°

A. K. Zhdanov and M. A. Sarkazov

In connection with the question of the optimal composition of water-alcohol mixtures for washing precipitates of binary and complex fluorides one of us [1] undertook the study of the equilibria in the ternary system water–ethylalcohol – sodium fluoride and showed that the solubility of sodium fluoride is diminished with increasing quantity of alcohol in the mixture. The results of the study of the equilibria in the system water – ethyl alcohol – ammonium difluoride at 25° are presented in the present communication.

Binary System Ammonium Difluoride – Water. The solubility of ammonium difluoride in water at various temperatures was studied by Spitsin, Sokolova, Popova and Zaring [2] and later by Yaltov and Polyakova [3]. The first investigators [2] determined the solubility of ammonium difluoride in 1 and 5% aqueous solutions of hydrofluoric acid at -20, -10, 0, 10, 20 and 50°. The second group of investigators [3] determined the solubility of ammonium difluoride in water at 0, 10, 20, 40, 60, 80 and 100°. They established that the solid phase at all temperatures in the binary system consisted of the anhydrous salt.

EXPERIMENTAL

Reagents. In the course of carrying out the present investigation we used reagents of a rather high degree of purity. Kahlbaum brand ammonium difluoride was used; alcohol rectificate was subjected to fractional distillation and its content in the distillate was established via measurement of the density. The solutions of other substances which we used for the analysis of the solutions and moist precipitates, as, for example, potassium dichromate, sodium thiosulfate, alkalis and acids, were prepared from chemically pure brand reagents. The water was twice redistilled.

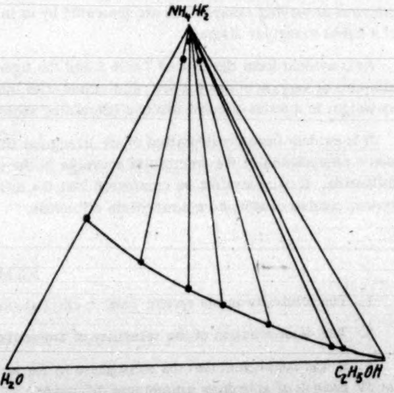
With the object of determining the solubility of ammonium difluoride in water at 25° and verifying the literature data, experiments were set up involving the determination of the solubility of this salt in water at 0, 25, 40 and 50° in a paraffined vessel. The values for the solubility of ammonium difluoride in water were calculated from the results of the analysis of the saturated solution for content of ammonium and fluorine.

In Table 1 along with our data for the solubility of ammonium difluoride in water at 0, 20, 40 and 60° are presented the data obtained by Yaltov and Polyakova [3].

TABLE 1

Solubility of Ammonium Difluoride in Water

Solubility (in % by weight)		
According to V.S.Yaltov and E.M.Polyakova	Our Data	Temperature
28.45	32.87	0°
37.56	—	20
—	43.73	25
50.05	53.03	40
—	54.15	50
61.00	—	60



Equilibrium in the water-ethyl alcohol-ammonium difluoride system at 25°.

It is evident from the data of Table 1 that the values obtained by us for the solubility of ammonium difluoride for 0 and 40° are higher than those of Yaltov and Polyakova [3]. As the ammonium difluoride used by us was of a high degree of purity, we are inclined to think that the low values for solubility of the difluoride obtained by Yaltov and Polyakova were due to the insufficient purity of the ammonium difluoride.

Preparation of Saturated Solutions of Ammonium Difluoride

The preparation of the saturated solutions of ammonium difluoride mixtures was carried out in a special vessel with a mercury seal. The study of the equilibria was begun with solutions containing a large quantity of alcohol and solid ammonium difluoride. The increase in the content of water in the mixture was achieved by introducing into the vessel of a definite quantity of bidistillate. Such a procedure for the study of the equilibria in the system was due to the fact that in the presence of alcohol fluorides have practically no action on glass. The quantity of water introduced into the vessel to prepare the saturated solutions of difluoride was calculated on the basis of the analytical data of the preceding test solution so that a solution with the assigned content of alcohol would be obtained.

The mixture was subjected to thermostating with constant intensive stirring for a duration of 6-8 hours, after which the solution in the vessel was let stand at the same temperature and the removal of a sample of the solution and the ground phase was carried out.

It was established by special experiments that the equilibrium in the system was reached after 4-5 hours of continuous stirring, and consequently subsequently the stirring for all samples was carried out for 6-8 hours.

At the same time that samples of the solution were removed for analysis, a sample of the solution was removed in a pyknometer to determine the density and also a sample of the moist precipitate to determine the composition of the solid phase by the residue method.

Methods of Analysis of the Solutions and Moist Precipitates. The solutions and moist precipitates were analyzed for their content of ethyl alcohol and ammonium difluoride. The content of water was determined by differences.

The determination of the alcohol content in the samples taken for analysis as well as of the solid phase was carried out by the iodometric method as in the preceding work [1]. The content of ammonium difluoride for the majority of samples was found by determination of ammonium and fluorine. For a small number of samples only, the ammonium was determined by a direct (distillation) method based on the titration with a standard solution of alkali of the excess of 0.1 N acid introduced which was left after absorption of the ammonia evolved from the sample under the action of alkali. The content of fluorine in the samples taken was determined by a modified Stark method [1].

DISCUSSION OF RESULTS

The results obtained by us for the determinations of the solubility of ammonium difluoride in water-alcohol mixtures of varying composition are presented by us in Table 2 and depicted graphically in the figure in the form of a Gibbs triangular diagram.

As is evident from the data of Table 2 and the figure, the solubility of ammonium difluoride in water-alcohol mixtures of varying composition is diminished with increasing quantity of alcohol in the mixture and reaches 1.73% by weight in a water-alcohol mixture containing about 90% alcohol, in place of 42.73% by weight in pure water.

It is evident from consideration of the triangular Gibbs diagram that all conoids of composition of the solution — composition of the precipitate converge in the corner of the diagram corresponding to 100% of ammonium difluoride. It can therefore be considered that the solid phase in the water — ethyl alcohol — ammonium difluoride system consists of anhydrous ammonium difluoride.

SUMMARY

1. The solubility in the system water — ethyl alcohol — ammonium difluoride at 25° was determined.
2. The determination of the solubility of ammonium difluoride in water at 0, 25, 40 and 50° was carried out.
3. It was established that the solid phase in the ternary system water — ethyl alcohol — ammonium difluoride at 25° consists of anhydrous ammonium difluoride.

TABLE 2

Equilibria in the Water–Ethyl Alcohol – Ammonium Difluoride System at 25°

Density of the solution (g/ml)	Composition of the solution (in % by weight)			Composition of the moist precipitate (in % by weight)			Ground phase
	Alcohol	Ammonium difluoride	Water	Alcohol	Ammonium difluoride	Water	
0.8118	88.21	1.73	10.06	0.60	95.13	4.27	NH_4HF_2
0.8302	84.80	2.95	12.25	0.53	93.62	5.85	
0.8514	75.90	5.02	19.08	0.52	95.41	4.07	
0.8716	73.24	6.53	20.23	0.99	94.88	4.13	
0.8979	63.97	11.17	24.86	5.57	90.34	4.09	
0.9395	49.69	16.53	33.78	1.95	90.63	7.42	
0.9813	37.55	22.19	40.26	1.95	95.03	13.02	
—	27.69	28.45	43.86	—	—	—	
—	21.47	30.47	48.06	1.45	96.82	1.73	
—	0.83	38.97	60.20	—	—	—	
—	—	43.73	56.27	—	—	—	

4. It was established that the solubility of ammonium difluoride in water-alcohol mixtures diminishes with increasing content of alcohol in the mixture and reaches at 25° a value of 1.73% by weight in the presence of 90% alcohol instead of 43.73% by weight in pure water.

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* See Consultants Bureau Translation, p. 773.

SOLUBILITY IN THE SYSTEM WATER – ETHYL ALCOHOL – SODIUM FLUORIDE AT 0 AND 25°

A. K. Zhdanov

It has been noted for some time now that the solubility of manv inorganic compounds in water is markedly diminished by addition of organic solvents, for example of alcohols, ketones and cetain other substances. This phenomenon has served as the basis for the utilization of organic solvents in chemical analysis. The sseparation of a whole series of salts is based on the differential solubility of them in various solvents [1 – 5].

In a number of cases water-alcohol mixtures find application in chemical analysis for washing precipitates which are appreciably soluble in water, with the object of washing them free from excess precipitant and other salts found in the mother liqouor and included in the precipitate. The best conditions for washing a precipitate must be considered such that the alcohol-water mixture employed to wash the precipitate hardly dissolves the precipitate but significantly dissolves the excess precipitant and other salts included in the mother liquor. It should be noted that in the question of the composition of the water-alcoholic mixtures which should be used to wash precipitates, empiricism is the rule and, in particular, literature data on the solubility of the fluorides of the alkaline metals,which are used as precipitants in photometric methods of analysis, are absent; consequently it is of interest to study the equilibria in the system water – ethyl alcohol – sodium fluoride and on the basis of the results obtained to proceed to the solution of the problem concerning the optimal composition of water-alcohol mixtures for washing the precipitates of binary and complex fluorides.

EXPERIMENTAL

Perparation of the Reagents. Sodium fluoride was prepared by neutralizing pure hydrofluoric acid with a solution of sodium hydroxide with phenolphthalein as the indicator with subsequent concentration of the sodium fluoride solution almost to dryness on an air bath. The precipitate which settled out was filtered through a porous filter, washed with bidistillate to the disappearance of the rose color, transferred into a platinum dish and dried in a drying chamber at 150°.

The alcohol rectificate was subjected to redistillation. The content of alcohol in the distillate was established by density measurements with the aid of a pyknometer at 25°.

The solutions of other substances necessary for carrying out the present investigation were prepared from chemically pure reagents. Certain of the reagents were additionally purified by recrystallization from bidistillate.

The water was twice redistilled.

Determination of the Solubility. The solubility in the system water – ethyl alcohol – sodium fluoride was determined at 0 and 25°.

The preparation of saturated solutions of sodium fluoride in water-alcohol mixtures was carried out in a special apparatus with a mercury seal.

The water-alcohol mixtures with varying compositions were prepared preliminarily in conical flasks with ground stoppers by mixing weighed quantities of water and alcohol. In all the flasks dry sodium fluoride was introduced in a quantity exceeding the magnitude of its solubility in water to obtain a saturated solution. The thus prepared solutions were kept for a prolonged time (1.5 – 2 months) at room temperature, with periodic shaking and then were transferred into an apparatus for the determination of the solubility and thermostated at constant intensive stirring for a duration of 6-8 hours, after which the removal of samples of the solution was carried out at the same temperature with a special pipet with a filtration glass plate sealed in it. In several cases samples of the ground phase were removed in preliminarily weighed containers.

Methods of Analysis of the Solutions and Moist Precipitates. The samples of the solution and ground phase taken were analyzed for content in them of ethyl alcohol and sodium fluoride. The content of water was determined by differences. To determine the content of sodium fluoride in the solution a weighed quantity of it was placed in a preliminarily weighed platinum dish and the concentration of the solution was carried out on a water bath to dryness and maintained in a drying chamber to constant weight at 150°.

The determination of the content of alcohol in the solution and the ground phase was carried out by an iodometric method based on the oxidation of ethyl alcohol in acidic medium by potassium bichromate to acetic acid and subsequent titration of the iodine evolved with thiosulfate.

The sodium fluoride in the ground phase was determined by analysis of the sample taken for fluorine by a modification of the Stark method: the fluorine was precipitated in the form of lead fluorochloride, the precipitate filtered off, washed and dissolved in nitric acid. The chloride ion evolved from the precipitate was titrated with 0.1 N $AgNO_3$ potentiometrically with a silver indicator electrode.

DISCUSSION OF RESULTS

The results obtained by us of the determinations for the solubility of sodium fluoride in water-alcohol mixtures of various compositions are presented in Tables 1 and 2 and depicted for 25° graphically (Fig. 1) on a Gibbs triangular diagram and on a rectangular diagram for the dependence of solubility of sodium fluoride on the concentration of alcohol in the mixture (Fig. 2).

As is evident from Fig. 1, all the conoids of composition of the solution-composition of the precipitate practically converge at the corner of the diagram corresponding to 100% NaF; it can consequently be considered that the solid phase in the system water – ethyl alcohol – sodium fluoride is anhydrous sodium fluoride.

TABLE 1

Equilibrium in the Water – Ethyl Alcohol – Sodium Fluoride System at 0°.

Density of the solution (g/ml)	Composition of the solution (% by weight)			Composition of the moist precipitate (% by weight)			Ground phase
	H_2O	C_2H_5OH	NaF	H_2O	C_2H_5OH	NaF	
1.0893	96.37	–	3.63	–	–	–	NaF
1.0871	88.10	9.70	2.20	–	–	–	
0.9880	77.89	20.88	1.23	23.23	5.63	71.14	
0.9706	69.50	29.80	0.70	–	–	–	
0.9523	59.00	40.60	0.40	14.06	10.44	75.50	
0.9258	46.48	53.26	0.26	–	–	–	
0.9018	38.67	61.30	0.03	13.40	8.18	78.42	
0.8623	18.60	81.38	0.02	–	–	–	

TABLE 2

Equilibrium in the Water – Ethyl Alcohol – Sodium Fluoride System at 25°

Density of the solution (g/ml)	Composition of the solution (% by weight)			Composition of the moist precipitate (% by weight)			Ground phase
	H_2O	C_2H_5OH	NaF	H_2O	C_2H_5OH	NaF	
1.038	96.15	–	3.85	–	–	–	NaF
1.007	87.48	10.11	2.41	29.14	4.34	66.52	
0.9798	77.81	20.81	1.38	22.53	7.44	70.03	
0.9572	71.04	28.31	0.65	26.31	10.50	63.19	
0.9312	57.13	42.47	0.40	–	–	–	
0.9131	42.05	50.54	0.31	16.22	17.64	66.14	
0.8912	40.15	59.71	0.14	–	–	–	
0.8764	32.28	67.64	0.08	10.43	25.36	64.21	
0.8446	27.63	72.33	0.04	–	–	–	
0.8175	17.44	82.54	0.02	–	–	–	

As is evident from Fig. 2, the solubility curve of sodium fluoride in water-alcohol mixtures initially falls steeply, to an approximate content of alcohol in the mixture of 40-50% by weight. Upon further increase in the content of alcohol in the mixture the angle of inclination of the curve is less and the curve itself proceeds more smoothly, showing that the solubility of sodium fluoride in the presence of such quantities of alcohol is practically slightly

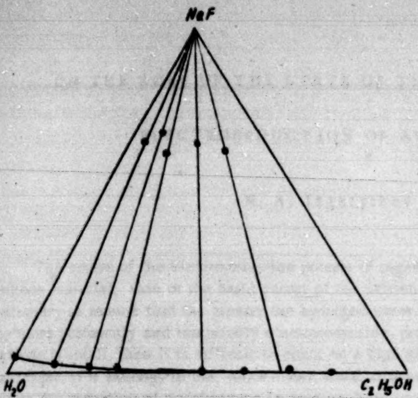

Fig. 1. Equilibria in the water – ethyl alcohol – sodium fluoride system at 25°.

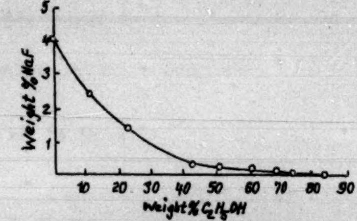

Fig. 2. Dependence of the solubility of sodium fluoride on the content of alcohol in the water-alcohol mixture at 25°.

changed. On the basis of the results obtained it is possible to come to the conclusion that for washing precipitates of binary and complex fluorides free from excess precipitant and other admixtures, water-alcohol mixtures containing 45-50% alcohol should be used if the washing is carried out with cooled mixture and 50-60% at temperatures significantly above 0°. To use water-alcohol mixtures with a greater content of alcohol for washing the precipitates is inadvisable since, in view of the insignificant solubility of sodium fluoride and other salts in strong water-alcohol mixtures, not all the admixture will be washed off. The density of the solutions of sodium fluoride in water-alcohol mixtures is diminished with increase in the percentage content of alcohol in the mixture. Since the solubility of sodium fluoride in water is small while it becomes still less in water-alcohol mixtures, the change in density of the solutions in the given ternary system is in accord with its change in the binary system water-alcohol.

SUMMARY

1. The solubilities of sodium fluoride at 0 and 25° were determined in the system water – ethyl alcohol – sodium fluoride.

2. It was established that the solid phase in the ternary system water – ethyl alcohol – sodium fluoride at 0 and 25° is sodium fluoride.

3. It was established that the solubility of sodium fluoride in water-alcohol mixtures diminishes with increasing alcohol content.

4. Since the solubility of sodium fluoride in water-alcohol mixtures containing more than 50% of alcohol is very small and practically is slightly changed upon further increase in the concentration of alcohol in the mixture, to wash precipitates of binary and complex fluorides free from excess sodium fluoride and other admixtures a water-alcohol mixture containing 50-60% of alcohol should be used.

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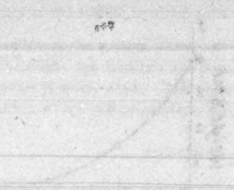

Fig. 2. [illegible] through the [illegible] content of alcohol in the [illegible] system

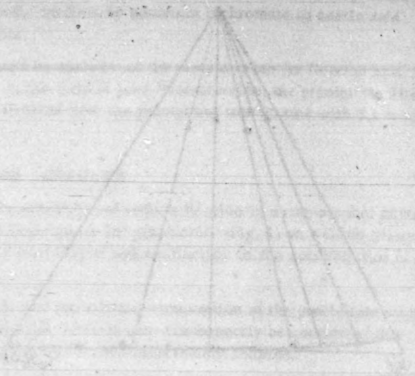

Fig. 1. Structure in the water – ethyl alcohol – sodium [illegible] system at 25°.

[illegible]

[illegible]

1. The solubilities of sodium [illegible] sodium [illegible]

2. It was established that the solid phase in the [illegible] is sodium [illegible]

3. It was established that the solubility of sodium [illegible]

[illegible]

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ON THE ROLE OF THE STATE OF THE SURFACE OF THE CATHODE IN THE ELECTROREDUCTION OF AROMATIC NITRO COMPOUNDS

N. A. Izgaryshev and M. Ya Fioshin

The course of the electroreduction process of organic ompounds depends to a large extent on the nature of the cathode material. One of the basic causes of the existence of this dependence is the hydrogen overvoltage. It is customary to assume that the greater the hydrogen overvoltage at the cathode, the higher its reducing properties, i.e., the more profoundly and intensively electroreduction process proceeds [1]. If the hydrogen overvoltage at the given cathode is small, then it is difficult to count on a high effectiveness of the reduction of organic depolarizers (in particular, if it belongs to the weak class), since at strong polarization the cathode begins to evolve hydrogen. Thus, during the reduction of nitrobenzene in acid medium on cathodes of zinc or lead the formation of aniline will proceed. By the use as cathode of platinum, the product of the incomplete reduction of nitrobenzene – phenylhydroxylamine [2] is formed. This is explained by the fact that at a platinum cathode the reduction potential of phenylhydroxylamine to aniline is more negative than the potential for the evolution of hydrogen; consequently in place of the reduction of phenylhydroxylamine the evolution of hydrogen will occur.

The direction and intensity of the process of electroreduction are determined not only by the nature of the cathode material.

Preliminary treatment of the cathode, consisting in placing on its surface a spongy (and in a number of cases dense galvanic) deposit of metals, pickling, mechanical treatment, etc. exerted a very substantial influence on the direction of the electroreduction process in a number of cases. Such preliminary treatment makes it possible to successfully reduce various organic compounds on metals with low hydrogen overvoltages. Tafel further noted the fact that on spongy lead the electroreduction proceeds with greater effectiveness than on smooth lead and proposed a method of special treatment of the surface of a lead cathode before the synthesis [3].

Lebedev and his coworkers in the course of a study of the electrohydrogenation of vinylacetylene, established that the process proceeds with excellent yields only on copper or brass cathodes covered with platinum black [4]. On smooth platinum the process proceeds poorly. There are indications concerning the role of preparing the surface of the cathode in the electrohydrogenation of acetylenic alcohols in the works of Favorskaya [5] and Lebedeva [6].

The preliminary placing of various metals on the surface of the cathode by the galvanic method which considerably increases its reduction capacity has a substantial significance in a number of cases. Thus, in the reduction of methylethylketone Izgaryshev and Aryamova successfully used a copper cathode having the form of a spiral, covered with electrolytic lead [7].

Preliminary treatment of the cathode, which facilitates the increase in the effectiveness of the reduction of organic substances does not always lead to the simultaneous increase of hydrogen overvoltage on the cathode. On spongy metals, for example, the hydrogen overvoltage is lower than on smooth metals, while the effectiveness of the electroreduction in a number of cases is considerably greater. At the same time the lowering of the hydrogen overvoltage on the spongy cathodes sometimes reaches 0.4 V, in comparison with smooth cathodes [8]. There are cases in which on both cathodes on which the hydrogen overvoltage is great, the electroreduction proceeds with high effectiveness, while on other cathodes, also with great hydrogen overvoltage, the reduction process proceeds very poorly. This can be seen in the case of the electroreduction of 2-chloromethyl-4-nitrotoluene into o-4-xylidene, studied by Berezovsky and Varkov [9]. These authors detected that the reduction of 2-chloromethyl-4-nitrotoluene proceeds with high yields on cathodes made of zinc and lead. The yield of o-4-xylidene is considerably lowered by the use as cathode of mercury or copper, and is entirely unsatisfactory when the reduction is carried out on a cathode of tin.

Apparently, the fact of the absence of a known relation between the hydrogen overvoltage and the effectiveness of the cathode reduction, established for a large quantity of syntheses, argues in favor of the catalytic influence of the surface of the cathode on the electroreduction of a number of organic depolarizers. The fact that the surface of the metal can exert catalytic influence on the cathodic and anode processes is discussed in the work of Pecherskaya and Stender [10].

The object of our work was the study of the electroreduction process of o-, m- and p-nitrobenzoic acids into the corresponding aminobenzoic acids on various cathodes. It is necessary to make the reservation that we did not pursue the goal of establishing the dependence of the yields of aminobenzoic acids on the nature of the cathode. The present investigation should be considered as an attempt to find the relation between the state of the surface of each of the cathodes investigated and the yields of aminobenzoic acids at various temperatures, concentration of hydrochloric acid and current densities. A brief note on the work already carried out has been published previously by us [11].

EXPERIMENTAL

Apparatus and Method of Investigation. The reduction of nitrobenzoic acids was studied on cathodes of tin, lead, amalgamated zinc, copper and graphite. The cathodes consisted of perforated cylinders which were placed in a porous cylindrical diaphragm, which served as a cathode space. The anode was prepared from sheet lead. The nitrobenzoic acid was introduced into the cathode space in the form of a suspension in hydrochloric acid. 15% sulfuric acid served as the anolyte in all cases. The suspension of nitrobenzoic acid was stirred with a mechanical stirrer. To maintain the determined temperature the electrolyzer was placed in a thermostat supplied with a thermoregulator. The yields of aminobenzoic acids were determined by diazotization. The measurement of the melting points of the aminobenzoic acids evolved from the catholyte after completion of the electroreduction process proved to be in excellent agreement with the literature data.

The study of the influence of the state of the surface of the cathode on the yields of aminobenzoic acids was carried out at various temperatures, current densities, concentrations of hydrochloric acid and added quantities of $CuCl_2 \cdot 2H_2O$. The reproducibility of the results of experiments carried out under identical conditions was excellent (1-2%).

1. Study of the Influence of Temperature. The nitrobenzoic acids in quantities of 5 g were reduced at various temperatures (20-75°) on cathodes of tin, lead, amalgamated zinc, copper and graphite. 2.32 N hydrochloric acid served as electrolyte, the current density at the cathode amounted to 8 A per square decimeter. In the reduction of the nitrobenzoic acids on cathodes of copper and graphite, good results could be obtained only in the presence of 1-7 g of $CuCl_2 \cdot 2H_2O$. The introduction of this additive facilitated the increase in the yields of aminobenzoic acids according to substance, but lowered their yields according to current, since to eliminate the Cu^{++} ions from the solution an additional quantity of electricity was passed, which was taken into account in the calculation of the yield by current.

In Table 1 are set forth the yields of aminobenzoic acids by substance at various temperatures.

TABLE 1

Yields of Aminobenzoic Acids by Substance at Various Temperatures on Various Cathodes

Temp.	Yield of acids (in %)														
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic				
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C
20°	65.7	48.8	68.0	68.7	–	91.6	60.1	72.3	72.8	42.6	29.3	5.4	–	–	–
30	94.5	81.4	87.8	73.2	38.4	96.7	69.4	90.1	75.4	52.2	38.9	13.0	–	11.4	18.2
40	98.0	88.2	96.5	65.2	42.6	95.6	85.1	90.9	73.2	83.3	51.6	34.2	–	28.5	43.7
50	99.0	86.9	97.3	52.6	42.9	97.0	84.8	95.0	–	74.5	63.4	67.1	–	46.4	76.8
60	98.5	85.4	97.5	48.7	–	97.2	85.8	94.8	84.3	62.4	93.4	87.9	–	69.1	66.9
70	97.7	84.2	97.3	–	–	92.2	77.8	95.1	82.7	50.4	94.6	88.1	–	78.4	70.4
75	96.8	–	97.8	–	–	90.1	–	94.7	80.6	–	95.3	84.7	–	73.8	70.9

Observations on the course of the syntheses showed that in the first instants after switching on the current a precipitate of copper is formed on cathodes of copper and graphite. This was particularly noticeable on graphite. The source of the copper which settled out on the copper and graphite cathodes was the Cu^{++} ions introduced into the catholyte in the form of the chlorous salt. With the use as cathode material of tin a considerable portion of the nitrobenzoic acids was reduced chemically, apparently, due to the reaction $Sn^{++} \rightarrow Sn^{++++}$.

It was indicated in one of the works that the yields of p-aminobenzoic acid on cathodes of tin and lead reached 98% only in the presence of 3-5 g of $SnCl_2 \cdot 2H_2O$ per 5 g p-nitrobenzoic acid [12]. We showed that it is in general possible to avoid the use of stannous chloride but at the same time is necessary to increase the intensity of stirring the suspension of p-nitrobenzoic acid by 3-4 times.

Apparently in the work of the above mentioned authors the intensity of stirring was insufficient for regular intake of p-nitrobenzoic acid at the cathode and its electrochemical reduction. The role of the introduced addition of $SnCl_2 \cdot 2H_2O$ probably consisted in the chemical reduction of that portion of the p-nitrobenzoic acid which, due to the insufficient effectiveness of the stirring, did not succeed in reaching the cathode. It is noteworthy that in all cases in which the cathode is formed of light sponge with a developed surface, the yields of aminobenzoic acids are increased, and, on the contrary, the formation of a dark precipitate on the surface of copper or graphite cathodes facilitates a marked reduction in the yields. The behavior of the lead cathode is very interesting. The study of the results of the synthesis on a lead cathode shows a considerable dependence of the yields of aminobenzoic acids on the temperature. This is probably associated with increased solubility of lead in hydrochloric acid with increased temperature. Since the unique source of the lead ions, by the discharge of which the formation of sponge on the cathode proceeds, is the material of the cathode, it is understandable that at higher temperatures the sponge will have a maximal surface. The increase in the effectiveness of the reduction in this case cannot be ascribed to anything other than the spongy structure of the surface of the cathode. The $^{++}$ participation of the Pb^{++} ions in the reduction reaction is excluded, since divalent lead does not have reducing properties. Attempts to reduce p-nitrobenzoic acid at a cathode of amalgamated zinc did not give positive results. This is explained by the fact that p-nitrobenzoic acid is poorly suspended in hydrochloric acid, while since upon dissociation of the amalgam there proceeds strong evolution of hydrogen, a foam is formed which is discharged from the electrolyzer and carries away particles of p-nitrobenzoic acid. The great losses of p-nitrobenzoic acid under these conditions distort the results and compelled us to withhold this isomer from reduction at a cathode of amalgamated zinc.

2. Study of the Influence of Additives. Additions of the salts of metals which facilitate the increased effectiveness of the electroreduction of organic substances, can be separated into 2 groups.

No particular doubts arise relative to the mechanism of action of polyvalent ions of the metals. Ions of the Ti^{+++}, Fe^{++}, Cr^{++}, V^{++++} type and others, introduced into the catholyte in the form of salts in which they have a lower valence, chemically reduce the organic substances and are thereby converted into the higher valence. At the cathode reduction of the ions of higher valence into ions of lower valence proceeds, which latter react anew with the organic substance etc. Such ions are sometimes called "hydrogen carriers" [13].

The salts of metals which belong to the other group (salts of zinc, mercury, lead and others) have another mechanism of action which consisted in precipitation at the cathode and increasing the hydrogen overvoltage, since it is well known that on zinc, mercury and lead the hydrogen overvoltage is great. The addition to the catholyte of salts of zinc, mercury, lead, can, for example, permit the reduction of nitrobenzene into aniline with excellent yields even at cathodes with low overvoltages where, in the absence of catalytic additives, the evolution of hydrogen [14] will chiefly proceed.

However, the question of the mechanism of action of these catalytic additives has still not been entirely clarified. For example, it is well known that upon the introduction into the catholyte of copper salts or powdered copper a marked increase in the effectiveness of the reduction of aromatic nitrocompounds occurs. This is explained by the fact that copper and also zinc or tin can be precipitated on the cathode and chemically reduce the nitrocompound to amine. Since in the reduction of aromatic nitrocompounds the most difficult stage which determines the rate of the entire process as a whole, is the conversion of the phenylhydroxylamine into the corresponding amine, it is assumed that zinc, tin or copper, precipitated at the cathode, specifically reduce phenylhydroxylamine, thereby increasing the rate of the process as a whole. The absence of complete clarity in the question of the influence of added salt on the process of electroreduction impelled us to study this question in the case of the nitrobenzoic acids. Particular attention was paid to the establishing of a relation between the yields of aminobenzoic acids by substance and the character of the deposits of metallic copper on the cathode. The cathodes were prepared from copper and graphite. The results of the experiments are presented in Table 2.

TABLE 2
Influence of Additions of Cuprous Chloride on the Yields of Aminobenzoic Acids by Substance on Copper and Graphite Cathodes

Concentration of $CuCl_2 \cdot 2H_2O$ (in g)	Yield of acids (in %)					
	o-Aminobenzoic		m-Aminobenzoic		p-Aminobenzoic	
	Cu (30°)	C (40°)	Cu (60°)	C (40°)	Cu (70°)	C (60°)
0	65.3	42.6	63.5	69.9	56.3	67.2
1	73.2	72.8	84.3	83.3	78.4	76.1
3	85.9	73.9	78.0	79.4	80.5	81.5
5	83.2	78.3	79.7	79.1	80.3	79.8
7	–	77.6	78.5	78.7	78.2	84.7

As has already been indicated, the introduction of additions of $CuCl_2 \cdot 2H_2O$ lowers the yield by current, since it increases the quantity of electricity consumed for the evolution of copper from the solution; consequently the introduction of additions of $CuCl_2 \cdot 2H_2O$ is expedient only in those cases when the effect in increasing the yields by substance justifies the additional consumption of electric energy. It is evident from Table 2 that in the majority of cases there exists some limit on the quantity of cuprous chloride introduced into the catholyte, above which no further increase in the yields of aminobenzoic acids by substance occurs. This is apparently explained by the fact that the duration of the electrolysis increases due to the time which is necessary to precipitate the copper from the solution. The increase in the duration of the electrolysis is associated with the emergence of undesirable side processes, in which intermediate and final products of the reduction of nitrobenzoic acids participate and which is associated with the observed reduction in the yields by substance on increase in the quantity of $CuCl_2 \cdot 2H_2O$ introduced into the catholyte.

3. Study of the Influence of the Concentration of Hydrochloric Acid. The data which characterize the yields of aminobenzoic acids at various concentrations of hydrochloric acid, are presented in Table 3.

In the majority of cases the change in the concentration of HCl is not appreciably reflected in the yields of aminobenzoic acids. Only o-nitrobenzoic acid appears to be an exception; during its reduction on a graphite cathode a fall in the yields of o-aminobenzoic acids with increase of HCl concentration is observed; at the same time a considerable quantity of side products appears in the catholyte. Evidently, this is 5-hydroxyanthranilic acid [15].

4. Study of the Influence of Current Density at the Cathode. The current density, as is well known, is an important factor on which very often depends the direction of the electroreduction process, and consequently, the nature of the end product.

The data of the influence of current density on the yields of aminobenzoic acids are presented in Table 4.

As is evident from the data of Table 4, the yields of aminobenzoic acids only slightly depend on the current density when tin and amalgamated zinc are used as the cathodes. This indicates the great rate of reduction of nitrobenzoic acids at a tin cathode, apparently due to the reaction $Sn^{++} \rightarrow Sn^{++++}$, i.e., due to chemical reduction.

TABLE 3

Yields of Aminobenzoic Acids by Substance at Various Concentrations of HCl on Various Cathodes

Concentration of HCl (N)	o-Aminobenzoic Acid					m-Aminobenzoic Acid					p-Aminobenzoic Acid			
	Sn (50°)	Pb (40°)	Zn + Hg (50°)	Cu (30°)	C (40°)	Sn (60°)	Pb (60°)	Zn + Hg (50°)	Cu (60°)	C (40°)	Sn (70°)	Pb (70°)	Cu (60°)	C (70°)
0.58	98.3	76.1	92.5	87.4	87.5	95.7	83.9	91.4	65.6	81.9	94.0	81.4	74.6	82.0
1.16	98.8	79.2	94.4	90.7	82.3	96.5	84.9	92.3	63.2	81.8	94.1	86.1	76.3	82.8
1.74	97.7	86.5	97.9	89.9	78.6	96.1	85.1	95.0	69.2	82.3	94.1	84.5	78.6	83.0
2.32	99.0	88.2	97.4	85.9	78.3	97.2	85.8	95.0	84.3	83.3	94.6	87.9	80.5	84.7
2.9	97.9	85.2	97.7	86.6	71.3	97.0	85.3	95.1	84.0	82.7	94.7	87.5	82.4	85.4
3.48	96.1	84.1	98.0	85.8	70.0	97.1	82.4	94.3	91.4	82.4	94.9	90.7	81.4	85.3
4.06	95.4	82.8	96.7	85.7	–	95.2	82.2	95.4	94.4	82.7	95.3	93.7	82.4	80.3

TABLE 4

Yields of Aminobenzoic Acids by Substance at Various Current Densities on Various Cathodes*

Current density at the cathode A/dm²	Yield of acids (in %)													
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic			
	Content of HCl (N)													
	2.32	2.32	2.32	1.16	0.58	2.32	2.32	2.32	4.06	2.36	2.32	4.06	2.9	3.48
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Cu	C
2	95.4	70.8	95.9	72.5	58.1	90.6	70.6	93.2	94.3	66.2	93.4	83.0	79.0	–
4	96.8	87.4	98.6	90.4	75.8	94.2	72.3	93.9	94.3	72.9	94.8	87.1	72.6	81.1
6	98.5	86.3	98.1	91.2	84.8	95.3	74.2	93.6	97.7	81.5	94.2	93.4	73.6	87.2
8	99.0	88.2	97.3	90.7	87.5	97.2	85.8	95.0	94.4	83.3	94.6	93.7	82.4	85.3
10	98.3	84.1	97.2	86.3	86.6	95.6	83.1	95.4	93.5	83.3	94.7	94.3	81.6	81.9
12	95.5	83.4	97.5	87.6	90.8	90.9	82.4	95.4	93.9	81.8	98.0	95.0	82.2	82.1
14	92.3	79.8	97.3	72.9	92.0	84.4	81.9	93.9	87.2	79.2	96.0	93.2	80.3	–

* The experiments were carried out at the same temperatures as in Table 3.

As regards a cathode of amalgamated zinc, reduction on it probably proceeds not as a result of the passage of a polarizing current, but basically due to decomposition of the amalgam. Electrons, freed by the decomposition of the zinc amalgam, enter into the reduction of the organic substance. A portion of the electrons is consumed by the evolution of hydrogen, which was also observed by us at the time of synthesis. Very interesting results were obtained at the lead cathode. In an already mentioned work [12] the authors reduced p-nitrobenzoic acid at a lead cathode and obtained a maximal yield at a current density of 6A per square decimeter in the presence of 5 g of $SnCl_2 \cdot 2H_2O$.

Increasing the number of rotations of the stirrer by approximately 3 times, we obtained such yields as in the mentioned work, but at a current density of 12A per square decimeter and in the absence of any additive. In the majority of cases diminishing the current density to 2A per square decimeter caused a drop in the yield of aminobenzoic acids due to increase in the electrolysis time and consequently, creation of favorable conditions for the development of side processes. An interesting fact which confirms the existence of a profound relation between the state of the cathode surface and the electroreduction process was noted during the reduction of p-nitrobenzoic acid at a copper cathode. At current densities of 4-6 A per square decimeter in the presence of 3 g of $CuCl_2 \cdot 2H_2O$ a dark precipitate is formed on the copper cathode which is accompanied by lowering of the yield of p-aminobenzoic acid. By reducing the current density to 2A per square decimeter in place of the expected further lowering of the yield an increase in it was observed, in spite of the fact that the electrolysis time was increased in comparison with the preceding experiment (at 4A per square decimeter) by 2 times. The increased yield of p-aminobenzoic acid at 2A per square decimeter, apparently, is facilitated by the dense, bright covering of copper, which is formed on the cathode. The "black" which is formed at the surface of the copper cathode at 4-6 A per square decimeter, probably lowers its activity to some extent.

DISCUSSION OF RESULTS

The results of the study of the process of electroreduction of nitrobenzoic acids under various conditions makes it possible to establish the existence of a relationship between the yields of aminobenzoic acids and the state of the cathode surface. On cathodes of graphite and copper in the absence of additions of $CuCl_2 \cdot 2H_2O$ we did not succeed in obtaining good yields of aminobenzoic acids. The most probable cause of this is the insufficiently high hydrogen over-voltage on copper and graphite. Copper ions, introduced into the catholyte, are destroyed at the cathode with the formation of a metallic precipitate. The effectiveness of the reduction depends on the form of the precipitate. The highest yields of aminobenzoic acids were achieved when a bright sponge having a developed surface, is formed on the cathode. The sponge on the surface of the cathode unmistakably shows catalytic action on the process of electroreduction. The mechanism of action of the sponge can, in our opinion, be represented in the following manner:

1. The finely dispersed sponge can chemically reduce the nitrobenzoic acids to aminobenzoic acids. Lukashevich showed that copper in a finely disperse state is capable of reducing nitrobenzene to aniline [16].

However the role of sponge in the electrochemical synthesis of organic compounds is not exhausted by participation in the process only as a chemical reductant. Lukashevich in the same work reported that finely disperse lead does not have high reducing properties and is capable of reducing nitrobenzene only to phenylhydroxylamine. The rate of the reduction of the latter to aniline is very small. The property of finely disperse lead, established by Lukashevich, clearly does not correspond with the results obtained by us in the electroreduction of nitrobenzoic acids on a spongy lead cathode. In those cases when a lead sponge appears on the cathode, the effectiveness of the reduction is increased and to a greater extent, the greater the volume of the sponge formed. Taking into account the fact that the hydrogen overvoltage on the sponge is less than on a smooth cathode, its role in the processes of electrochemical reduction of organic substances may be determined otherwise than in the first case.

2. In organic syntheses copper in the finely disperse state is widely used as a catalyst [17]. The role of the catalyst consists in lowering the activation energy of the reaction due to adsorption of molecules of the organic substance on the surface of this catalyst. The greater the surface of the catalyst, the higher its capacity for adsorption. During the adsorption there takes place deformation of the molecules of the organic substance which proceeds under the action of the force field of the catalyst surface. The deformation leads to disruption of the bonds in the molecule and to increase in its reactivity [18]. It was established that copper and lead catalyze the reaction of chemical reduction of nitrobenzene into aniline in which the reducing agent is hydrogen. The use of finely disperse lead makes it possible to obtain aniline in a yield equal to 97% [19].

The spongy surface of the cathode responds as well as possible to the demands presented to the active catalysts. On a spongy cathode surface adsorption of molecules of nitrobenzoic acids proceeds and leads to their deformation which is manifested in increase in the dipole moment constant. In a comparison of the dipole moments of many organic substances with the reduction potentials of these substances Voitkevich detected that with increase in the dipole moment the reduction potential becomes more positive, i.e., the depolarizing action of the substance is increased [20]. Thus, increase in the dipole moment which proceeds as a result of the adsorption of nitrobenzoic acid molecules apparently appears to be one of the basic causes of the increase in the effectiveness of reduction on a spongy cathode.

On the basis of the experiments carried out certain conclusions concerning the mechanism of the electroreduction process can be drawn. The concept of taking into account the nature of the cathode material in the processes of electroreduction of organic substances obtained its greatest development in the works of Antropov [21]. By a comparison of the null potential charge of several metals with the reduction potentials of a number of organic substances on cathodes of these metals, Antropov established that the organic depolarizer is well reduced only if the reduction potential is not markedly different from the null potential charge (for example for Zn, Hg, Pb). Antropov explained this situation by the fact that the molecules of the organic substance are adsorbed on the cathode only in the region directly adjacent to the potential of the null charge. If the reduction potential is far removed from the potential of the null charge (Pt, Ag, Ni), the reduction proceeds poorly and is accompanied by the evolution of hydrogen. We have already reported concerning the measurement of the reduction potential of nitrobenzoic acids on various cathodes [22]. It was established that on cathodes of lead, tin and mercury the reduction potentials of nitrobenzoic acids differ little from the null potentials of the charge of these metals. On smooth cathodes of copper and graphite the difference between the reduction potentials and the null potentials of the charge reaches considerable magnitudes. The high effectiveness of the reduction on cathodes of graphite and copper covered with copper sponge, is apparently explained by the fact that as a result of adsorption an increase in the dipole moments of the molecules of nitrobenzoic acids occurs which leads to lowering of the activation energy of the process and which is manifested in diminishing of the reduction potentials and their approximation to the null potentials of the charge of the metals. The reduction of nitrobenzoic acids is, apparently, a primary electrode act which consists in the transfer of electrons from the cathode directly to the electropositive center of the nitrogroup with subsequent participation of hydrogen ions in the formation of the amino group.

SUMMARY

1. The electroreduction process of nitrobenzoic acids to aminobenzoic acids on cathodes of tin, lead, copper, graphite and amalgamated zinc was studied.

2. It was established that the state of the cathode surface plays a substantial role in the electroreduction of nitrobenzoic acids. The maximal yields of aminobenzoic acids were obtained when a lead or copper sponge was formed on cathodes of copper, lead or graphite. It can be assumed that the electroreduction of nitrobenzoic acids on these cathodes is of a catalytic nature.

3. Several assumptions concerning the mechanism of the process of electroreduction of aromatic nitrocompounds were made. The electroreduction process of compounds of this class is, apparently, a primary electrode act.

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ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH

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The solution of the problem of the mechanism of electrode processes during the electroprecipitation of metals from solutions of their complex salts can not be accomplished without detailed study of the composition and properties of the complex ions which are found in the electrolyte. This situation is of a general character and, consequently in studying the possibility of the galvanic precipitation of copper from pyrophosphate bath we encountered the necessity of specially considering the question of its composition.

It is necessary to note that in the last few years a number of investigations of the composition and stability of complex ions of copper pyrophosphate have appeared. The analysis of the available data permits the following conclusions to be made.

Depending on the pH and concentration of the components, when solutions of copper sulfate and sodium pyrophosphate were mixed the following ions were detected: $[Cu(P_2O_7)]^{-2}$; $[Cu(P_2O_7)_2]^{-6}$; $[Cu(HP_2O_7)(P_2O_7)]^{-5}$; $[Cu(HP_2O_7)_2]^{-4}$; $[Cu(P_2O_7)(OH)]^{-3}$. The first two complexes appeared as a result of the general complex formation reaction and naturally participate in solvation equilibria of the type [1]:

$$[Cu(P_2O_7)_2]^{-6} + xH_2O \rightleftharpoons [Cu(H_2O)_y]^{+2} + 2[P_2O_7(H_2O)_z]^{-4}$$

$$[Cu(P_2O_7)]^{-2} + xH_2O \rightleftharpoons [Cu(H_2O)_y]^{+2} + [P_2O_7(H_2O)_z]^{-4} .$$

The instability constant of the $[Cu(P_2O_7)_2]^{-6}$ ion has been determined by many investigators! Stabrovsky [2] cited the value $K_{inst.} = 3.1 \cdot 10^{-10}$, Rogers and Reynolds [3] $K_{inst.} = 2 \cdot 10^{-11}$ and, finally Waters and Aaron [4] $K_{inst.} = 2 \cdot 10^{-9}$. There are many contradictory data for the instability constants of the $[Cu(P_2O_7)]^{-2}$ ion.

As is well known from the literature data, both complexes under consideration can exist in the pH range approximately from 7 to 10 [4]. In addition, there is an indication [4] of the existence of the complexes $[Cu_2P_2O_7]^0$ and $[Cu_4(P_2O_7)]^{+4}$, but these ions, apparently, are only formed in very dilute solutions.

In a number of cases the solvation equilibria in copper-pyrophosphate solutions can be complicated by side reactions of the acid-base type.

Thus, at pH > 10 the following equilibrium takes place:

$$[Cu(P_2O_7)]^{-2} + H_2O \rightleftharpoons [Cu(P_2O_7)(OH)]^{-3} + H^+.$$

Similiar complex cuprate-pyrophosphate anion was detected by a number of authors [5,6] and its instability constant was equal, according to their data, to $6 \cdot 10^{-14}$ or $2 \cdot 10^{-16}$.

At pH > 11 the copper-pyrophosphate complex is destroyed and a precipitate of cupric oxide hydrate settles out.

In acidic solutions equilibria are possible which lead to the formation of complex copper-pyrophosphate ions containing the $(HP_2O_7)^{-3}$ group. At pH 5.3-7.0 the formation of the ion $[Cu(HP_2O_7)(P_2O_7)]^{-5}$ with an instability constant of 10^{-10}[6] was noted, while at pH < 5.3 the ion $[Cu(HP_2O_7)_2]^{-4}$ with an instability constant close to $4 \cdot 10^{-7}$ [6] was noted. The study of the latter complexes was complicated in connection with the fact that in acid solutions a precipitate of the hypothetical composition $Na_2Cu_3(P_2O_7)_2$ settled out [6].

As is evident from the information set forth on the stability of copper pyrophosphate complexes, there is one very substantial hiatus in them — this is the sharp discrepancy of the available data on the instability constant of the $[Cu(P_2O_7)]^{-2}$ complex. At the same time, the precise knowledge of this quantity is necessary to elucidate the concrete picture of the composition of the copper-pyrophosphate solutions of varying concentration. Its knowledge is also important for the solution of the question of the mechanism of electrode reactions in a copper-pyrophosphate bath.

To fill this gap we calculated the instability constants of the complex ions $[Cu(P_2O_7)_2]^{-6}$ and $[Cu(P_2O_7)]^{-2}$ on the basis of analysis of the data on the measurement of the potentials of a copper electrode in the corresponding solutions.

The potentials were measured by the usual compensation method with the methodology not differing from that generally adopted [7].

The results of the indicated measurements are set forth in Table 1.

In the calculations of the instability constant we start from the equations:

$$K_1 = \frac{[P_2O_7^{-4}][Cu^{+2}]}{[Cu(P_2O_7)^{-2}]} \quad \text{and} \quad K_2 = \frac{[P_2O_7^{-4}]^2[Cu^{+2}]}{[Cu(P_2O_7)_2^{-6}]}$$

When the excess of $P_2O_7^{-4}$ ions is so great that one can assume the formation almost exclusively of $[Cu(P_2O_7)_2]^{-6}$ ions, the concentration of these ions is practically equal to the initial concentration of copper (C^0_{Cu}), while $[P_2O_7$ is respectively equal to the initial concentration of pyrophosphate after deducting $2C^0_{Cu}$. Thus $[Cu^{+2}] = \frac{K_2C^0_{Cu}}{C^0_{P_2O_7}-2C^0_{Cu}}$,

and therefore

$$E-E^0_{Cu} = 0.03 \log \frac{K_2C^0_{Cu}}{C^0_{P_2O_7}-2C^0_{Cu}} = 0.03\,[\log K_2 + \log C^0_{Cu} - \log (C_{P_2O_7} - 2C^0_{Cu})] \qquad (1)$$

Evidently, when the initial concentration of pyrophosphate is close to the initial concentration of copper, the formation of the complex $[Cu(P_2O_7)_2]^{-6}$ is difficult to expect and then

$$E-E^0_{Cu} = 0.03\,[\log K_1 + \log C^0_{Cu} - \log (C^0_{P_2O_7}-C^0_{Cu})]. \qquad (2)$$

It should be noted that the available literature data for K_1 are either such that K_1 is approximately equal to K_2, or they correspond to the inequality $K_2 \ll K_1$. In the first case the conditions for fulfilling equation (1) are in general difficultly attainable. On the other hand, the conditions for fulfilling equation (2) can be obtained comparatively readily. They correspond to the first 5 systems set forth in Table 1.

TABLE 1

Potentials of a Copper Electrode in the System $CuSO_4-Na_4P_2O_7-H_2O$ and the Instability Constants of the Copper-Pyrophosphate Complexes at 25 °C

System no.	Concentration (in moles)		Assumed predominant form	E (in volts)	$\log K_{inst.}$
	$CuSO_4$	$Na_4P_2O_7$			
1	0.0050	0.0050	$[Cu(P_2O_7)]^{-2}$	+0.198	−7.4
2	0.0100	0.0100		+0.219	−6.3
3	0.0200	0.0200		+0.222	−6.3
4	0.0200	0.0300		+0.172	−6.0
5	0.0300	0.0500		+0.162	−6.2
6	0.0050	0.0300	$[Cu(P_2O_7)_2]^{-6}$	+0.035	−9.8
7	0.0200	0.1000		+0.011	−10.6
8	0.040	0.100		+0.052	−10.2
9	0.040	0.200		-0.010	−10.5
10	0.20	0.500		+0.004	−11.5

The data of Waters and Aaron prove to correspond more with the actual conditions and therefore equation (1) can also be used in the determined limits.

Thus the obtained value for K_1 is $0.63 \cdot 10^{-6}$ and for K_2 is $0.5 \cdot 10^{-10}$. The values found for K_2 are found in agreement with the data of other authors [2,3] and the ratio of the constants satisfies the Babko-Khodakov condition [9]:

$$\frac{\log K_2 - \log K_1}{\log K_1} = \frac{P_2 - P_1}{-P_1} \qquad (3)$$

where P_1 and P_2 are the energetic characteristics of the complexes, equal to -8 and -14 respectively [10].

Actually, if K_1 is approximately equal to 10^{-6}, then according to equation (3)

$$\log K_2 = \frac{14+8}{8}(-6) = -1.75 \cdot 6 = -10.50.$$

On the basis of the obtained values of the instability constants a graph of the dependence of the contents of various complex forms in solution on the concentration of free pyrophosphate can be constructed.

The calculation was carried out according to the equations:

$$\left.\begin{aligned}&[Cu^{+2}] = \frac{100\%}{1 + \dfrac{[P_2O_7^{-4}]}{K_1} + \dfrac{[P_2O_7^{-4}]^2}{K_2}}\\ &[Cu(P_2O_7)^{-2}] = [Cu^{+2}]\frac{[P_2O_7^{-4}]}{K_1};\quad [Cu(P_2O_7)_2^{-6}] = [Cu^{+2}]\frac{[P_2O_7^{-4}]^2}{K_2}.\end{aligned}\right\}\qquad (4)$$

The results of the calculation are presented in Fig. 1; it follows from its data that the concentration of the $[Cu(P_2O_7)]^{-2}$ anion is maximal only in a narrow interval of values for the concentration of $[P_2O_7^{-4}]$, and this form in the best case contains only 50% in all of copper and generally can not predominate; it is therefore clear that the calculated value of the instability constant K_1 is somewhat low, but this has no further theoretical significance and it can be confirmed that the ratio $\log K_2 : \log K_1$ is close to 2 in each case.

Such a conclusion is in complete agreement with the data of Waters and Aaron [4]. Its verification can be accomplished by means of the determination of the conductance of the system $CuSO_4-Na_4P_2O_7-H_2O$. The measurements were carried out by the usual method with the aid of a variable current bridge.

The temperature was held at 20 ± 0.2°. The results of the measurements are presented in Table 2 and in Fig. 2 and bear witness to the existence of points of inflexion on the curves $\kappa = f(C)$, corresponding to the condition $[Na_4P_2O_7] : [CuSO_4] = 3 : 2$.

TABLE 2

Conductance of the System $CuSO_4-Na_4P_2O_7-H_2O$ at 20°

Concentration (in moles)		κ, ohms⁻¹ cm⁻¹	Concentration (in moles)		κ, ohms⁻¹ cm⁻¹
$CuSO_4$	$Na_4P_2O_7$		$CuSO_4$	$Na_4P_2O_7$	
0.020	0.020	0.0045	0.020	0.080	0.0134
0.020	0.025	0.0058	0.020	0.090	0.0242
0.020	0.030	0.0069	0.030	0.060	0.0094
0.020	0.035	0.0072	0.040	0.060	0.0083
0.020	0.040	0.0078	0.040	0.080	0.0123
0.020	0.045	0.0085	0.040	0.100	0.0160
0.020	0.050	0.0091	0.040	0.200	0.0240
0.020	0.060	0.0104	0.050	0.060	0.0111
0.020	0.070	0.0118	0.050	0.100	0.0153

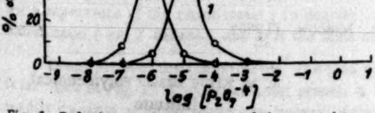

Fig. 1. Relative concentrations of the complex forms in the system $Cu^{+2}-P_2O_7^{-4}$
1) $[Cu(P_2O_7)]^{-2}$, 2) $[Cu(P_2O_7)_2]^{-6}$, 3) $Cu(H_2O)_n^{+2}$

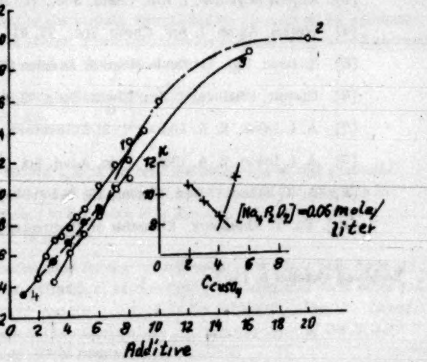

Fig. 2. Influence of complex formation on the conductance.
1) 0.02 m. $CuSO_4 + Na_4P_2O_7$, 2) 0.04 m. $CuSO_4 + Na_4P_2O_7$
3) 0.01 m. $CuSO_4 + Na_2C_2O_4$, 4) 0.02 m. $CuSO_4 + Na_3C_6H_5O_7$.

As can be concluded without difficulty, this point closely coincides with the point a on Fig. 1 and almost completely coincides with the transfer of copper into the $[Cu(P_2O_7)_2]^{-6}$ ion. The presence of such an inflexion is readily explained by the data obtained for the instability constant of the complex ions of copper pyrophosphate.

Thus, the results of the investigation show that under ordinary conditions the predominant ion in copper-pyrophosphate complex electrolyte is the $[Cu(P_2O_7)_2]^{-6}$ ion. Inasmuch as the working conditions for a pyrophosphate bath are characterized by the following data: pH 7.5–9.0, $[Na_4P_2O_7]:[CuSO_4] \geq 2$, this ion is practically uniquely capable of participating in the cathode process since the concentration of all other forms of the complex compounds is extraordinarily small.

Another important conclusion from the data obtained consists in the fact that with further refinements in the pyrophosphate bath a ratio of concentrations $[Na_4P_2O_7]:[CuSO_4] < 2$, should be obtained, since under these conditions the nature of the stimulating ions is scarcely changed while the lowering of the concentration of free pyrophosphate presents a greater perspective, inasmuch as in this case the crystallization of the $Na_4P_2O_7$ salt at the surface of the cathode becomes scarcely probable [8]. The ensuring of a sufficiently satisfactory solubility of the anodes during the electrolysis can be achieved by addition to the electrolyte of sodium citrate and other side substances which form quite soluble but not very stable complexes with copper. A similar ratio of concentrations of $CuSO_4$ and $Na_4P_2O_7$ with simultaneous introduction of substances which form collateral complexes in practice was accomplished by us and led to completely satisfactory results.

SUMMARY

1. The question of the composition of complex ions in a real pyrophosphate electrolyte, suitable for galvanic copper plating was considered.

2. The instability constants of complexes of copper pyrophosphate were measured potentiometrically. The values found for K_1 were $0.63 \cdot 10^{-6}$, and for K_2, $0.5 \cdot 10^{-10}$.

3. The dependence of the conductance of the system

$$CuSO_4-Na_4P_2O_7-H_2O$$

on the concentration of the components was studied. An inflexion point on the conductance curves, which corresponded to practically complete transfer of copper into the complex ion, was detected.

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INVESTIGATION OF THE STRUCTURAL CHANGES IN IRON-NICKEL-ALUMINUM ALLOYS BY THE TRUE HEAT CAPACITY METHOD

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In spite of numerous investigations [1,2] up to the present time there has been no consensus of opinion on the origin in iron-nickel-aluminum alloys of a high coercivity. Some [3] consider that the anomalously high coercivity (Hc) is caused by ordering processes of the high temperature phase β', others [4,5,6] by its dispersion decomposition into the phases β and β'. Tretyi [7] assumes that in the dispersed solid the austenite α-phase also participates. A number of other questions, which are undoubtedly of practical importance, also remain unexplained. On the composition diagram of the system Fe – Ni – Al the boundaries of the concentration region of existence of the high coercivity alloys are not specified, the thermodynamic properties of the phases of this region are not clear, and the structural changes involved in achieving the high coercivity alloys are not established.

The present work is devoted to the study of the structural changes in Fe – Ni – Al alloys in the process of their magnetic hardening (increased coercivity), and to the establishment of the relation of these changes to the changes in magnetic properties. The investigation was carried out by the true heat capacity method.

As is well known, the method of true heat capacity is one of the most sensitive methods of investigating the changes in the physical state of a solid body. With its aid, a considerable variety of the forms of conversion which take place in solid phases has been detected. In a whole series of metallic systems the presence of so called conversions of the second type which include the changes associated with the processes of ordering, ageing, appearance and disappearance of magnetic properties, etc. was shown.

The method of true heat capacity also permits the quantitative evaluation of the conversion heat effects which proceed in solid alloys and makes it possible to judge concerning the rates of these conversions.

To evaluate the magnetic state, the coercivity (H_c) of the experimental sample was measured by a ballistic method.

EXPERIMENTAL

Principles of the Method of Determining the True* Heat Capacity. The measurement of the true heat capacity was carried out by a method, similar in principle to the method worked out by Moser [8] and Sykes[9].

The essential part of this method consists in the fact that to the sample, surrounded on all sides by an adiabatic envelope, is continuously transmitted electric energy of known power. The time intervals corresponding to a determined small increase in the temperature of the sample are accurately read at the same time.

The true heat capacity (C_p) of the experimental sample is calculated from the equation:

$$C_p = \left\{ \frac{(Q \pm \alpha\Delta\theta)\Delta\tau}{\Delta t} - K \right\} \cdot \frac{1}{m},$$

where Q is the heat transmitted to the calorimeter (in cal./second), α is the heat exchange coefficient (in cal/ second · degree), $\pm\Delta\theta$ is the average deviation from the conditions of adiabaticity (in degrees); Δt is the rise in the temperature of the calorimeter (in degrees), $\Delta\tau$ is the time (in seconds), K is the heat value of the empty calorimeter (cal./ degree), and m is the mass of the sample (in grams).

Description of the Calorimeter. The plan of the calorimeter used for the measurement of the true heat capacity, is set forth in Fig. 1. The calorimeter proper, B, consists of two cylindrical barrels tightly entering into each other and readily capable of being withdrawn internally and externally and rigidly fixed in the adiabatic jacket A. Above, the calorimeter was covered with the cover C. All the portions of the calorimeter (with the exclusion of the bottom of the external barrel which was turned out of silver) were made out of heat resistant steel**.

The adiabatic jacket A consisted of a massive silver barrel with a cover consisting of two screw-on portions. In the wall of the lower portion of the barrel were drilled vertical canals in which the thermometric leads leading from the calorimeter B passed. The heat necessary to heat the sample under adiabatic conditions, was supplied with the aid of the heater W.

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* By true heat capacity is understood the average heat capacity measured in a narrow temperature range.

** The composition of the steel (in%) was Cr 25, A -5.5; Ti 0.3; C 0.04 and Fe 69.16.

The heater consisted of a double wound nichrome spiral (resistance approximately equal to 6 ohms) welded to a nichrome stand (d = 1 mm), which was hammered out within the calorimeter in plates. The whole system was heated on a tubular electric furnace with a double wound winding (not shown in the figure). The measurement of the temperature was accomplished with the aid of a gold-palladium-platinum thermoelement. The thermoelectromotive force of the thermocouples and the electric energy supplied to the heater were measured by the compensation method (on a Disselhorst compensator). A mirror galvanometer with a sensitivity of $2.5 \cdot 10^{-8}$ A and a coil resistance of 6 ohms served as null instrument.

Subjects of the Investigation and Thermal Treatment. Alloys of the following composition (in atoms%) were investigated:

54.8 Fe,	23.3 Ni,	21.9 Al	[alloy (sample)1]
55.7 Fe,	21.0 Ni.	23.3 Al	[alloy (sample)2]
35.0 Fe,	25.4 Ni,	39.6 Al	[alloy (sample)3].

The first two alloys on the composition diagram of the system Fe – Ni – Al (Fig. 2) [10] are distributed in the two-phase β + β' region. They go over into the monophasic state at a temperature of approximately 970 ° [11].

As is well known, it is possible to obtain anomalously high coercivity in alloys of the β + β' region.

Alloy 3 is found in the β' region. According to the literature data, alloys of this region are not capable of magnetic hardening. The true heat capacity of the final states was studied for each alloy: biphasic, after tempering, monophasic, after quenching. The intermediate states also are of especial interest – the transition state from biphasic to a monophasic melt, – inasmuch as they ensure a maximally high coercivity of the alloy [2].

The tempering of the samples was carried out in a vacuum at 800° for 18 hours with subsequent slow (5 degrees/hour) cooling to 400°. The thermal treatment to obtain a monophasic melt was accomplished by cooling the sample at 1300° in water. The quality of the quenching was controlled by measuring the coercivity of the quenched sample. After quenching, the coercivity of sample 1 amounted to 14±1 oersteds and of sample 2, 50 oersteds. We did not succeed in quenching samples with H_c less in magnitude.

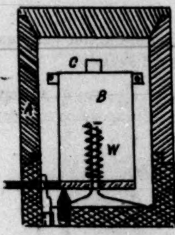

Fig. 1. Plan of the calorimeter. Explanation in the text.

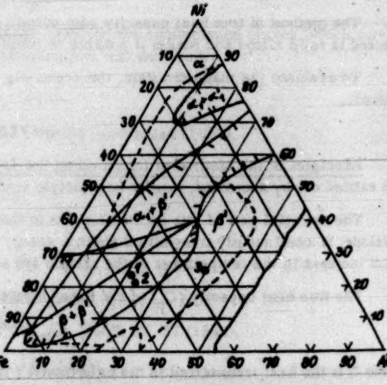

Fig. 2. Composition diagram of the system Fe – Ni – Al, according to Bradley (in atoms %) [10].

The intermediate states were fixed, on the one hand, by the quenching of a biphasic alloy at various temperatures (620, 800°) in water and on the other hand, by a process of repeated adiabatic heatings (in the tempering process) of a sample quenched a minimal coercivity. The heating was repeated until the sample under investigation became maximally coercive (H_c = 250 oersteds).

All the measurements of the true heat capacity were carried out up to 700° with a precision of 1-1.5%.

Results of the Measurements of the True Heat Capacity of Sample 1. The results of the measurements of the true heat capacity of sample 1 are set forth in Fig. 3. The curves were drawn with the experimental points obtained for each 2-4° taken into account (but the technical causes are not shown in the figure).

The heat capacity of the tempered sample (curve a) increases right up to 500° with a temperature coefficient ($\frac{dC_p}{dt}$ that is normal in magnitude. The heat capacity is practically constant in the range 450-550°, changes again in the 600° region with a value of the coefficient $\frac{dC_p}{dt}$ that is normal in magnitude and, finally, above 615° an anomalous change in the heat capacity is observed.

The diminishing of $\frac{dC_p}{dt}$ in the 450-550° regions indicates the presence of a process which is accompanied by a weak exothermic effect (see below).

The behavior of the sample close to 600° can also characterize the presence of a conversion associated with evolution of heat. This conversion can be caused both by further tempering of the melt (inasmuch as carrying out the tempering at 800° can be insufficient) and by coagulation of the already evolved β and β' phases.

The curves b,c and e_1 were obtained after quenching the tempered sample respectively at 620, 800 and 1300° and thus characterize the behavior of a biphasic alloy in the course of assuming the monophasic state.

As is evident, quenching introduces significant changes into the structure of the tempered sample. One must, however, differentiate quenching at 620 and 800° (temperature of existence of the biphasic region β + β') and at 1300° (temperature of existence of the solid solution β').

The curves b and c, which characterize the behavior of the biphasic sample after quenching at 620 and 800°, are similar to each other. Each of them indicates the presence in the sample of two conversions which proceed with the evolution of heat: one in the 300-450° region, another in the 450-550° region.

The curve e_1, which reflects the behavior of the monophasic solid solution β', is considerably different from the curves b and c. It has only one minimum in the 300-450° region which is in common with curves b and c. A minimum in the 450-550° region is not observed while a minimum appears in the 580-650° region which is particularly characteristic.

In what follows, the effects pertaining to conversions in the 300-450, 450-550, 580-650° region will be respectively designated as low, middle and high temperature effects.

The curve e_1 completes the series of curves a, b and c which characterize the behavior of the biphasic sample in the process of assuming the monophasic state. At the same time it is the curve of the first heating in the series of curves e_1, e_2 and e_3 (Fig. 3). These curves were obtained in the process of repeated adiabatic heatings of the sample, quenched at minimal coercivity (approximately equal to 14 oersteds), and therefore characterize the energetic changes in the minimally coervive sample during its transition into a state with high coercivity.

The data of the H_c measurements, before and after each heating, are presented in Table 1.

TABLE 1

No. of heating	Alloy after quenching at 1300° in water			
	1		2	
	H_c (oersted)		H_c (oersted)	
	Before expt.	After expt.	Before expt.	After expt.
1	51.0	233.0	14.1	136.0
2	233.0	250.0	136.0	191.5
3	250.0	250.0 max.	191.5	216.3
4	–	–	216.3	226.0
5	–	–	226.0	226.0 max.

Curves e_2 and e_3 reflect the behavior of a minimally coercive sample, respectively during a second and a third heating.

It follows from the curve of secondary heating, e_2, that the quenched sample still does not undergo conversion in the 300-450° region. Conversion takes place in the 580-650° region, although the effect of this conversion is expressed considerably more weakly than on curve e_1.

The fact that a middle temperature exothermic effect, characteristic only of the biphasic state (curves a,b, and c) appears on curve e_2 is very curious.

A high temperature exothermic effect is entirely absent on the curve of the third heating, e_3, and an effect in the middle temperature region (450-550°) occurs only as on curve e_2. It is characteristic that the third heating, in contrast to first two heatings, is not accompanied by change in the coercivity (Table 1). This means that curve e_3 reflects the energetic behavior of the maximally coercive sample.

On the basis of the analysis indicated above of the curves of Fig. 3, we can assert that the sample under investigation undergoes (in principle) the same conversions (low temperature, middle temperature and high temperature) regardless of whether it proceeds from the biphasic to the monophasic (curves a, b, c and e_1) or from the monophasic (minimally coercive) to the highly coercive state (curves e_1, e_2 and e_3).

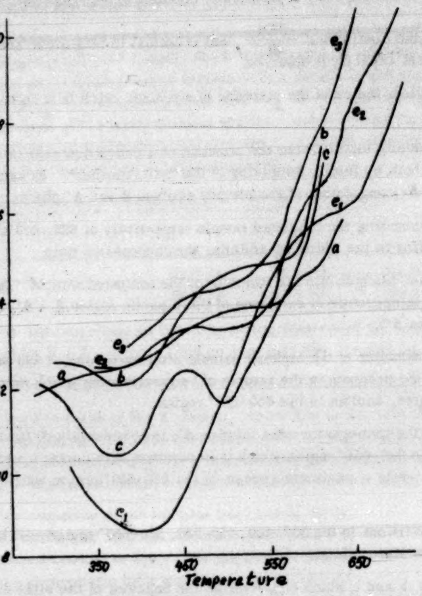

Fig. 3. Curves for the true heat capacity as a function of the temperature of alloy 1 after various heat treatments.
a) After tempering at 800° (18 hours); b) and c) after quenching the tempered sample; e_1) e_2) and e_3) curves of the first second and third heatings of a sample, quenched at 1300° in water.

We must now determine which of the indicated conversions is associated with the process of magnetic hardening of Fe – Ni – Al alloys.

Let us return to the comparison of the results of measurements of the true heat capacity (curves e_1, e_2, and e_3) and the coercivity of the intermediate states (Table 2) of the sample, obtained in the course of the secondary adiabatic heatings. It follows from this comparison that the energetic conversions in the region of low (300-450°) and middle (450-550°) temperatures do not directly participate in the magnetic hardening of iron-nickel-aluminum alloys. The coercivity of the sample hardly changes while being heated right up to 500°. The increase of H_c occurs in the region of the high temperature exothermic effect, this effect is appreciably weakened with each subsequent heating. A lesser increase in the coercivity (Table 2) corresponds to a lesser exothermic effect. As has already been indicated, on the curve e_3, which reflects the behavior of a maximally coercive sample, the high temperature exothermic effect is practically absent.

Thus, of the three conversions which have been brought to light, only the conversion in the region of high temperatures (580-650°) is a necessary condition for establishing a highly coercive state in Fe – Ni – Al melts.

We link the low temperature exothermic conversion with the effect of supplementary ordering of the high temperature β' phase. The correctness of this assumption is confirmed, in the first place, by the fact that this conversion is strictly localized (300-450°) and in the second place, since this conversion can be observed in a sample by quenching it at various temperatures (620, 800, 1300°), the higher the quenching temperature, the greater the heat effect corresponding to it (curves b, c, and e_1).

In our opinion, the high temperature heat effect is a consequence of decomposition of the high temperature phase into conjugated phases. The following important facts argue in favor of this assertion.

1. A sample, which has undergone high temperature conversion (for example, after the first heating), is capcable of undergoing a conversion characteristic of the biphasic state, and specifically middle temperature conversion (curves e_2, and e_3).

2. The high temperature heat effect occurs only in samples quenched at a temperature at which the monophasic solid solution exists (above 970°). In samples quenched at temperatures at which the biphasic β+β' region exists, we did not observe such a conversion.

The experimental material obtained does not permit the nature of the middle temperature conversion to be definitely determined. There is no doubt that it is a consequence of processes associated with the formation of conjugated phases from the decomposition of the monophasic solid solution.

Results of the Measurements of the True Heat Capacity of Sample 2. : The results of the measurements of the true heat capacity of sample 2 are set forth in Fig. 4. The curves, like those of Fig. 3, are drawn on the basis of the experimental points.

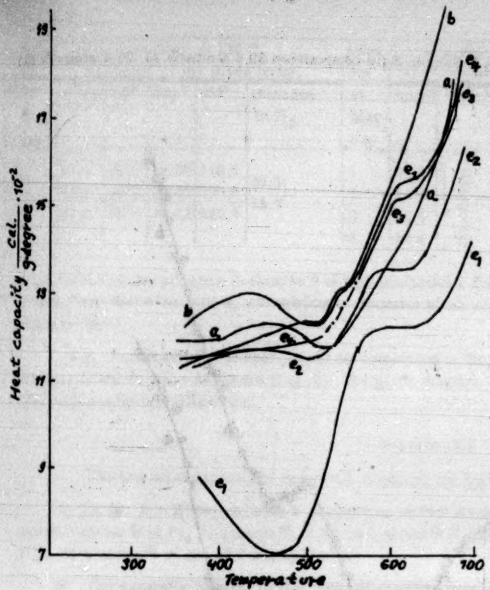

Fig. 4. Curves for the true heat capacity as a function of the temperature of alloy 2 after various heat treatments.
a) After tempering at 800° (18 hrs.); b) after casting; e_1, e_2, e_3, and e_4) the corresponding curves of the first, second, fourth, and fifth heatings of a sample, quenched at 1300° in water.

By analogy with sample 1, curve a characterizes the energetic behavior of a tempered sample, while curves e_1, e_2, e_3, e_4 reflect the energetic changes in a sample, quenched at minimal coercivity (50 oersteds) in the course of the secondary adiabatic heatings.

It can readily be seen that curves a and e_1 do not qualitatively differ from the corresponding curves of sample 1. The differences which are present amount only to the fact that the heat effects caused by the low temperature and high temperature conversions are more sharply expressed on the curves of sample 2.

Energetic changes analogous to those of sample 1 are also reflected on curves e_2, e_3 and e_4.* Sample 2 also did not undergo conversion in the low temperature region on second heating (curve e_2); the conversion in the high temperature (580-650°) is retained and conversion is observed in the middle temperature region (450-550°). Each subsequent heating (curves e_1, e_2, e_3, e_4) is characterized by a high temperature heat effect which is weaker in comparison with the preceding and a smaller increase in the value of H_c (Table 2).

However, the kinetics of the decomposition of the high temperature solid solution β', and consequently, the conditions of the magnetic hardening of samples 1 and 2 is appreciably different. In the first place, the maximum possible coercivity for sample 2 is reached with the least speed (four heatings as against two ** for sample 1); in the second place, the total heat effect of the high temperature region exceeds that of sample 1, since the considerable increase in coercive force expected in this connection for sample 2 was not observed. H_c was of the same order for both samples. In the third place, finally, the high temperature conversion effect noted on curve e_4 is not associated, as one was bound to expect, with the change in coercive force (Table 1); curve e_4 as well as curve e_3, Fig. 3 in fact reflects the state of a maximally coercive sample.

The absence of increase in the coercivity as a result of the fifth heating (curve e_4) of sample 2 should be explained by the presence in it of processes which completely compensate for the action of the high temperature conversion, such as, apparently, coagulation of phases β and β' and the relieving various forms of tension. An appreciable increase in these processes for sample 2 was facilitated by a more prolonged tempering than for sample 1.

Thus, the high temperature conversion is only a necessary, but not a sufficient condition for the establishment in Fe-Ni-Al alloys of maximal coercivity. Conditions, in which there are processes which compensate for the action of the high temperature conversion, must be acknowledged, apparently, as sufficient. We assume that the conditions of magnetic hardening during continuous quenching of the sample at a certain critical rate approach such conditions. This thermal treatment, as is well known, permits one to achieve maximal coercivity. It is therefore of interest to return to the analysis of curve b, Fig. 4, which reflects the energetic behavior of a highly coercive (approximately 370 oersteds) sample obtained by casting.

Curve b is characterized by one heat effect in the middle temperature region (450-550°); the high temperature heat effect is actually absent. In form, curve b brings to mind the curve (e_3 of Fig. 3) of the highly coercive sample 1, which, as we demonstrated, is, in comparison with sample 2, less subject to the influence of processes which compensate for the action of high temperature conversion.

The similarity of curves b and e_3 also argues in favor of the conclusion that no kind of difference (in principle) between the structures of the highly coercive samples, obtained under the conditions of quenching and tempering, and in the process of continuous cooling, is observed.

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* e_3 and e_4 are respectively the curves of the fourth and fifth heatings. The curve of the third heating is not shown on Fig. 4.

** The rates of heatings were identical.

Curves of the True Heat Capacity of Sample 3. Sample 3 (in composition 39.6 atoms % Al, 25.4 atoms % Ni) is decomposed in the monophasic region of Bradley (Fig. 2).

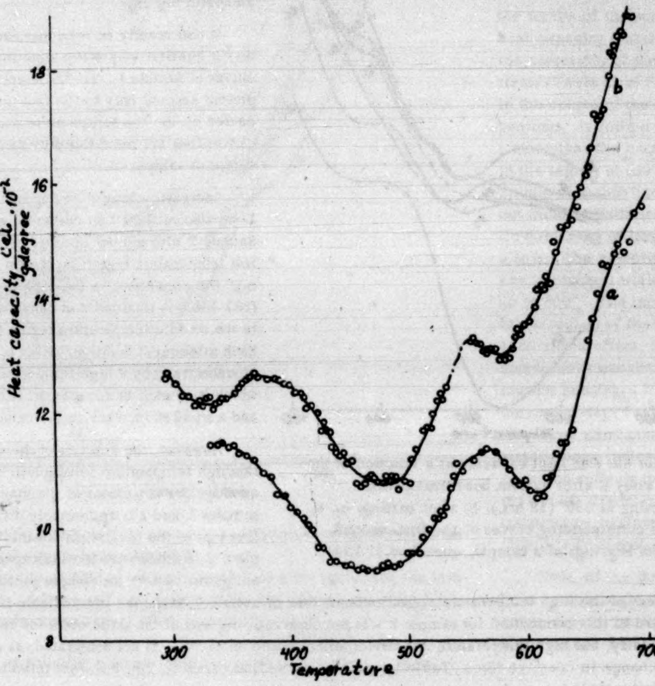

Fig. 5. Curves for the true heat capacity as a function of the temperature of melt 3.
a) Sample quenched at 1300° in water; b) sample tempered at 800° (length of heating 5 hours).

The curves for the true heat capacity of sample 3 are set forth in Fig. 5. Curve a was obtained by heating the sample, quenched at 1300° in water, curve b with the same sample, but held at 800° for a duration of 5 hours and quenched at this temperature in water.

The shape of curve a brings to mind the curves for other samples quenched at 1300° in water (curves e_1 Fig. 3 and 4). In accordance with these, the heat effect in the 350-500° region should be ascribed to a supplementary ordering of the high temperature β' phase and the effect observed in the 550-660° region, to its decomposition. The given hypothesis is found to be in complete agreement with the results of the measurements of the coercivity. Prior to heating the coercivity of the sample was determined to be 4 oersteds and, after heating it rose to a value of 140 oersteds. We assume that when quenched, sample 3 undergoes precipitation hardening with evolution of the same excess phase as samples 1 and 2.

Curve b also brings to mind one of the curves of biphasic state of the alloys under consideration. In the low temperature region (up to 550°) it was qualitatively close to curve c of Fig. 3, since it is characterized by heat effects which are caused by low and middle temperature conversions. The quantitative differences in the comparable heat effects of curves b and c, and also the displacement of the minimums of the heat effects on curve b in the direction of lower temperatures argues only for differing compositions and quantitative ratios of the decomposed phases.

In the high temperature region, curve b is close in its shape to curve e_4 (Fig. 4). As in the latter, curve b reflects the behavior of a maximally coercive sample (H_c before and after heating is equal to 158 oersteds) and at the same

TABLE 2

Alloy 1 after quenching at 1300°						Alloy 2 after quenching at 1300° in water					
No. of heating	H_c (oersteds) at the given temp.					No. of heating	H_c (oersteds) at the given temp.				
	Room	515°	620°	703°	Increase in H_c		Room	515°	620°	703°	Increase in H_c
1	51.0	51.0	58.00	190.0	30.0	1	14.4	No change	14.9	86.5	49.5
2	51.0	55.0	69.00	220.0	12.7	2	14.4		18.0	136.0	23.7
3	51.0	56.7	74.16	232.7		3	14.4		20.0	159.7	
						4	14.4		24.0	178.0	18.3

times indicates the presence in sample 3 of high temperature conversion. Apparently, the magnetic hardening of this sample, like that of sample 2, was subject to processes which compensate for the action of the high temperature exothermic effect.

Thus, the behavior of sample 3 does not correspond to the monophasic composition plotted on the composition diagram of the Fe–Ni–Al system (Fig. 2). The given diagram, in spite of the changes which were introduced in 1951 [12], requires further refinement.

SUMMARY

1. The true heat capacity of tempered, quenched and highly coercive melts was studied:

a) in the $\beta + \beta'$ region, with a composition of 54.8 atoms % of Fe, 23.3 atoms % of Ni, 21.9 atoms % of Al, and 55.7 atoms % of Fe, 21.0 atoms % of Ni, 23.3 atoms % of Al; and b) in the β' region with a content of 35.0 atoms % of Fe, 25.4 atoms % of Ni; 39.6 atoms % of Al.

2. The energetic changes in the course of reaching iron-nickel-aluminum alloys of high coercivity state were considered.

3. The presence of three exothermic conversions in the 300-450, 450-550 and 580-650° region was noted.

4. It was established that a conversion in the 580-650° region was associated with processes of magnetic hardening of iron-nickel-aluminum alloys.

5. It was shown that the boundaries of the $\beta + \beta'$ region of the composition diagram of the Fe-Ni-Al system requires further refinement.

6. The region of precipitation hardening of Fe-Ni-Al alloys was rendered more precise; specifically, it was placed above 550°. Processes were observed in the sample which were accompanied by low and middle temperature effects and which did not directly participate in the magnetic hardening of these melts.

7. The experimental data do not permit us to note any differences in principle between the energetic states of the highly coercive samples obtained in the process of quenching and tempering and under conditions of continuous cooling.

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INVESTIGATIONS IN THE FIELD OF POLYTHIONIC ACIDS

IV. SULFURIZATION OF HEXATHIONIC ACID

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Hexathionic acid, formed as a result of the reaction of free thiosulfuric acid and hydrogen sulfide according to the equation

$$3H_2S_2O_3 + H_2S \longrightarrow H_2S_6O_6 + S + 3H_2O, \qquad (1)$$

adds a certain quantity of elementary sulfur and, thus, is partially converted into polythionic acids of a higher degree of sulfurization. We recently succeeded in showing that in the solutions obtained as a result of the indicated reaction, octathionic acid is present [1]. However, its quantity in such solutions is very small, since the sulfurization of hexathionic acid, i.e., the reaction of the products of reaction 1 proceeds on a very limited scale: the average content of sulfur in the molecule of the polythionic acid obtained does not reach more than 6.5.

In the present work we have set ourselves the task of accomplishing the sulfurization of hexathionic acid on as large a scale as possible and of obtaining solutions containing predominantly acids with more than six sulfur atoms in the molecule.

EXPERIMENTAL

1. Preparation of solutions of polythionic acids with an average number of sulfur atoms in the molecule, n, equal to approximately 7. The first method by which it proved to be possible to accomplish the task indicated above, involved carrying out reaction (1) in concentrated hydrochloric acid in the presence of sulfurous acid. The optimal molar ratio of the starting materials – thiosulfate : sulfide : disulfite was 3:1:2.

150 ml of concentrated (10.5-12N) hydrochloric acid was cooled in a flask with a ground stopper to a temperature below 10°. A solution of 16 millimoles of $NaHSO_3$ in 20 ml of water was carefully poured into this acid, and the flask was at once covered. In another vessel a solution of 24 millimoles of $Na_2S_2O_3$ in 20 ml of water was stirred with a concentrated solution of sulfide containing 8 millimoles of KHS or Na_2S. This mixture was carefully distributed from a submerged pipet into the mixture of hydrochloric acid and bisulfite. On shaking a white crystalline precipitate (NaCl or KCl) at once appeared, and quickly settled out. After several minutes an opalescence – the beginning of sulfur evolution – appeared. In the course of 15-20 minutes the reaction mixture was diluted in a measuring flask with 5 N hydrochloric acid to 250 ml, corked and left in a cooled place (approximately 10°). After 15-16 hours a sample was taken from the transparent upper layer of the solution to determine the hydrosulfuric acid. The remaining mixture was filtered through a dry weighed filter into a dry vessel. The sulfur which was filtered off was dried in a desiccator and weighed and the mother liquor was subjected to analysis for sulfur compounds [2].

It is evident from the experimental data (Table 1) that a solution of polythionic acid is formed in this way, the composition of which approximately corresponds to that of heptathionic acid; therefore one could expect that heptathionic acid in the form of its benzidine salt could be obtained from such a solution.

We carried out the fractional precipitation of the polythionic acids with benzidine chloride from the solutions of experiments 4 - 7 and determined the average number of sulfur atoms in the molecule of the benzidine salt preparations obtained [1]. It is evident from the data presented (Table 2) that fraction I of the precipitate consisted of octathionate in all cases and II, of the hexathionate of benzidine. We did not succeed in obtaining heptathionate.

It follows from this that the solutions with n approximately equal to 7 obtained by the above method, primarily contain octathionic and hexathionic acid, in approximately equal quantities, but do not contain appreciable quantities of heptathionic acid. The latter, evidently, if it exists in general, must be in a very stable equilibrium with both other acids.

It is interesting that fraction III of the benzidine salt precipitate again consists of octathionate. This fraction is evolved after addition to the mother liquor from Fraction II of excess benzidine chloride and being left to stand for

3 - 4 days in a cooled place. It follows from this that after eliminating a considerable portion of the octathionic acid (fraction I of the benzidine salt) a slow accumulation of the latter proceeds anew in the solution, probably via redistribution of sulfur between molecules of polythionic acids, for example, according to the equations:

$$\begin{gathered} 2H_2S_6O_6 \longrightarrow H_2S_5O_6 + H_2S_7O_6 \\ H_2S_7O_6 + H_2S_6O_6 \longrightarrow H_2S_8O_6 + H_2S_5O_6 \\ 3H_2S_6O_6 \longrightarrow H_2S_8O_6 + 2H_2S_5O_6. \end{gathered} \qquad (2)$$

The basic reaction leading to the formation of polythionic acids under the conditions described above should be considered reaction (1), since the number of moles of polythionic acids found in all cases was equal to about one third of the number of moles of thiosulfate taken or somewhat less. Consequently, the polythionic acid which is primarily formed here, appears to be hexathionic acid. Sulfurous acid undoubtedly participates in its sulfurization to octathionic acid, since in the absence of the latter this sulfurization proceeds only on a small scale among the starting materials [1].

TABLE 1

Products of the Reaction of 24 Millimoles of $Na_2S_2O_3$, 8 Millimoles of KHS and 16 Millimoles of $NaHSO_3$ in Concentrated HCl

Experiment No.	Content (in millimoles) of $H_2S_nO_6$	Content (in millimoles) of $H_2S_2O_3$	Content (in millimoles) of SO_2	Content of elementary sulfur (in mg-atoms)	Number of sulfur atoms n
1	7.05	1.50	13.24	5.78	7.25
2	8.13	1.25	10.00	–	7.00
3	7.50	5.00	12.70	5.42	6.83
4	7.87	0.50	15.28	2.60	6.84
5	6.56	1.25	14.53	5.20	7.06
6	6.69	1.25	14.66	4.25	7.07
7	8.12	–	14.06	–	6.90

TABLE 2

Average Number of Sulfur Atoms (n) in the Molecule of Benzidine Polythionates (Experiments 4-7) after Fractional Precipitation

Experiment No.	Number of sulfur atoms Fraction I	Number of sulfur atoms Fraction II	Number of sulfur atoms Fraction III
4	8.1	6.1	8.0
5	8.0	6.2	8.0
6	8.1	–	–
7	8.2	–	–

Sulfurous acid here plays, evidently, the role of sulfur carrier: it first adds elementary sulfur, freed as a result of reaction (1),

$$H_2SO_3 + S \rightleftharpoons H_2S_2O_3, \qquad (3)$$

while the thiosulfuric acid which is formed gives up, under the given conditions of acidity, a sulfur atom to the hexathionic acid

$$H_2S_6O_6 + 2H_2S_2O_3 \rightleftharpoons H_2S_8O_6 + 2SO_2 + 2H_2O. \qquad (4)$$

The latter reaction probably proceeds in two stages, i.e., via the unstable heptathionic acid.

Reaction (3) can proceed from left to right under the conditions of our experiments, since the free thiosulfuric acid has a considerably greater stability in relation to the ordinary decomposition with elimination of sulfur [3]. The remarkably high hydrogen ion concentration also appears to be a prerequisite for the formation of octathionic acid according to equation (4), i.e., the displacement of this equilibrium is to the right.

Experiments 8 and 9, carried out under completely analogous conditions, but with the use of 2 N hydrochloric acid in place of concentrated hydrochloric acid (Table 3) illustrate this role of the hydrogen ion concentration.

Here too, the primary reaction in the formation of polythionic acid is undoubtedly the reaction of thiosulfuric acid with hydrogen sulfide according to equation (1), since the number of moles of polythionic acid formed amounts to around one third of the number of moles of thiosulfate taken and is almost equal to the number of moles of sulfide taken. But here, in place of the sulfonization of hexathionic acid, its so-called sulfite decomposition to pentathionic acid occurs according to the equation

$$H_2S_6O_6 + H_2SO_3 \rightleftharpoons H_2S_5O_6 + H_2S_2O_3. \qquad (5)$$

Inasmuch as the thiosulfuric acid here regenerated is unstable in dilute hydrochloric acid, we find considerably more elementary sulfur in these experiments than equation (1) requires, and almost all the initial sulfurous acid.

TABLE 3

Products of the Reaction of 48 Millimoles of $Na_2S_2O_3$, 16 Millimoles of KHS and 32 Millimoles of $NaHSO_3$ in 2N HCl

Experiment No.	Content (in millimoles), of			Content of elementary sulfur (in mg-atoms)	Number of sulfur atoms n
	$H_2S_nO_6$	$H_2S_2O_3$	SO_2		
8	15.0	7.0	28.7	26.6	5.20
9	15.6	3.1	30.3	26.9	4.95

2. Preparation of solutions of octathionic acid.

In the experiments described above, sulfurization of hexathionic acid proceeds due to the elementary sulfur freed as a result of reaction (1); therefore the heptathionic acid or the mixture which we obtained of equivalent quantities of octathionic and hexathionic acids here represent the theoretical limit of sulfurization.

With the object of exceeding this limit we attempted to accomplish in one and the same solution the two basic reactions – reaction (1), giving hexathionic acid and sulfur and simultaneously the reaction of hydrogen sulfide with sulfurous acid.

$$2H_2S + H_2SO_3 \longrightarrow 3S + 3H_2O. \qquad (6)$$

We started at the same time on the assumption that the additional quantity of sulfur which reaction (6) would give could, although partially, add to the hexathionic acid which was being formed as a result of reaction (1).

The experimental data (Table 4) show that, starting with a molar ratio of the reagents – thiosulfate : sulfide: bisulfite of 6:7:5, with a small excess of bisulfite, * we succeeded in obtaining a solution containing almost all the sulfur of the starting materials (up to 98%) in the form of polythionic acids with an average number of sulfur atoms in the molecule n = 8.

TABLE 4

Reaction of Thiosulfate, Sulfide and Bisulfite with Hydrochloric Acid

Experiment No.	Amount taken of				Concentration of HCl (N)	Volume of the mixture (in ml)	Reaction products				Number of sulfur atoms n
	$Na_2S_2O_3$	NaHS	$NaHSO_3$	HCl (in ml)			$H_2S_nO_6$	$H_2S_2O_3$	SO_2	S (in mg-atoms)	
	(In millimoles)						(In millimoles)				
10	24.0	27.75	22.85	300	1.6	500	11.50	0.50	0.69	0.63	7.97
11	24.0	27.75	22.85	300	1.6	500	10.75	1.00	0.62	1.95	7.91
12	24.0	28.00	25.00	300	2.0	500	12.25	0.25	3.06	1.17	7.93
13	120.0	138.80	105.80	700	3.4	1000	59.0	3.50	2.75	Traces	8.00
14	120.0	140.00	116.00	700	3.4	1000	59.5	3.00	2.40	Traces	8.00
15	120.0	138.80	105.80	700	3.4	1000	59.9	0.50	1.70	Traces	8.00
16	60.0	70.00	56.00	300	5.0	500	29.4	4.00	1.80	Traces	7.80
17	60.0	70.00	52.40	300	5.0	500	29.5	0.00	1.75	Traces	8.00
18	60.0	70.00	58.00	300	5.0	500	29.0	3.00	4.25	Traces	7.90

The experimental methods of these experiments were analogous to those described above for experiments 1-9 with only this difference, that here it was not necessary to let the reaction mixture stand for a prolonged time, since sulfur was almost not evolved at all or was evolved only in a small quantity and quickly precipitated. In this case it proved expedient to carry out the reaction not in a concentrated but in moderately dilute hydrochloric acid solution. The dilution of the reaction mixture could be carried out with water in a measuring flask. At the optimal concentration of hydrochloric acid (3.4-5 N, experiments 13-18), sulfur was hardly evolved at all, and sometimes only a light opalescence appeared while the solution acquired a yellowish color.

Precipitation of polythionic acid from these solutions with benzidine chloride gave benzidine octathionate (Table 5); we did not succeed in obtaining any other polythionates of benzidine by fractional precipitation in this case. It follows from this that these solutions predominantly contain octathionic acid, which has considerable stability under the given conditions.

The circumstance, that solutions of octathionic acid prepared under optimal acidity conditions (3.4-5 N HCl, experiments 13-18) remain transparent for 4-5 hours, and, after 2-3 days at a temperature not exceeding 10°, evolve only an insignificant quantity of sulfur, also indicates the comparative stability of octathionic acid.

The number of moles of octathionic acid formed in these experiments exceeds by one third the number of moles of thiosulfate taken. Consequently, the formation of polythionic acid here proceeds not only via reaction (1), but also as a result of the reaction of hydrogen sulfide with sulfurous acid, as in the well known Vakenroder solution. The general

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* Excess bisulfite was necessary in view of the fact that at the time of the experiment a small quantity of sulfur dioxide volatilized.

i.e., the total process can be expressed by the equation:

$$6H_2S_2O_3 + 7H_2S + 5H_2SO_3 \longrightarrow 3H_2S_8O_6 + 15H_2O \tag{7}$$

Our experimental data, in particular the results of experiments 13-18, carried out at optimal solution acidity, are found to be in entire agreement with this equation: the number of moles of octathionic acid found is almost exactly equal to half the number of moles of the thiosulfate taken and almost all the sulfur of the starting materials is found in the form of this acid.

TABLE 5

Number of Sulfur Atoms in the Benzidine Polythionates from Experiments 16-18

Experiment No.	n
16	8.0
17	8.02
18	8.0

Equation (7) can be obtained by the addition of a series of simple equations, which still express well known reactions; specifically, equations (1), (3), (4), (6), and also:

$$H_2S + H_2SO_3 \rightleftharpoons H_2S_2O_2 + H_2O \tag{8}$$

and

$$H_2S_2O_2 + 2H_2S_2O_3 \longrightarrow H_2S_6O_6 + 2H_2O\ [4]. \tag{9}$$

The mechanism of reaction (1) has already been analyzed by us previously [1].

A somewhat simpler overall expression for the formation of octathionic acid from these same substances can be obtained by another combination of these same equations:

$$5H_2S_2O_3 + 4H_2S + 2H_2SO_3 \longrightarrow 2H_2S_8O_6 + 9H_2O \tag{10}$$

The quantitative completion of the reaction according to this equation, however, can not be accomplished except at an initial ratio of the reacting substances of 5:4:2, since the evolution of considerable quantities of sulfur can not be successfully avoided.

SUMMARY

1. The reaction of thiosulfuric acid with hydrogen sulfide in concentrated hydrochloric acid in the presence of sulfurous acid leads to the formation of a solution of polythionic acid which corresponds in its composition to heptathionic acid, but which consists of a mixture of octathionic and hexathionic acids.

2. Thiosulfuric acid, hydrogen sulfide and sulfurous acid react almost quantitatively in moderately dilute hydrochloric acid to form octathionic acid.

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CERTAIN THERMODYNAMIC PROPERTIES OF SULFUR IN LIQUID IRON-SULFUR ALLOYS SATURATED WITH CARBON

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The thermodynamic properties, in particular the activity, of sulfur dissolved in liquid iron and the influence on it of various elements (C, Cu, Si, P, Al and others) have been determined by a number of investigators from data of the chemical equilibrium of an alloy with the gaseous phase [1]. It was discovered that the Fe–S system is characterized by positive deviations from the laws of ideal solutions. Additions of carbon intensify these deviations; this is explained by the appearance of a region of stratification of the liquids. It turned out, for example that at 2.3% C the coefficient of activity of sulfur is doubled while in alloys saturated with carbon, it is increased 6 times [2].

It was of interest to follow the behavior of sulfur in alloys saturated with carbon, in the entire Fe–FeS composition range, since no such investigations have been carried out. With this object, the method of electromotive forces, which has thoroughly proved its value in sulfide systems [3,4] was used.

In following this method, the concentration chain which follows was set up

$$\ominus\ \mathrm{Fe, S, C_{saturated}}\ \big|\ \mathrm{CaO, Na_2O, Na_2S, SiO_2}\ \big|\ \mathrm{Fe, 35\%S, C_{saturated}}\ \oplus$$

The content of sulfur at one of the electrodes was varied from experiment to experiment from 0.048 to 33%, while it was kept constant and equal to 35% S at the other electrode.

Alloys of varying composition were prepared from synthetic cast iron (4.4% C, 0.08% Mn, 0.1% Si, 0.03% S), the material of the comparison electrode was (35% S, 0.1% Si, 0.2% Mn, 0.15% C). They were fused at a temperature of 1250° in a graphite crucible under a layer of wood charcoal while being constantly stirred. The concentration of carbon in the alloys containing up to 0.71% S, varied from 4.5 to 3.5% C and did not markedly differ from that calculated according to the empirical [5] formula

$$[\%C] = 1.19 + 0.00262\,t - [\%S]\ \{1.67 - 0.001 \cdot (t - 1200)\}. \qquad (1)$$

An alloy of composition: 72% SiO_2, 17% Na_2O, 9% CaO, 2% NaS_2, served as electrolyte. It was obtained by fusing glass with sodium sulfide in a graphite crucible. The experiments were carried out at a temperature of 1250°. The electrolyzer was made of refractory clay. The construction of the electrolyzer and also the methods of the measurements were similar to those previously described [6].

Since the activity of carbon was identical at both electrodes, while there were no iron ions in the electrolyte, the only process which determined the potential was the conversion of sulfur:

$$S_{\mathrm{electrode}} + 2\ominus = S^{2-}_{\mathrm{electrolyte}} \qquad (2)$$

In this connection the electromotive force of the element must be determined only by the ratio of sulfur in the alloys:

$$E = \frac{RT}{2F} \ln \frac{a^{0}_{S}}{a_{S}} \qquad (3)$$

We can calculate the value of a_S with the aid of equation (3) if we assume that in the most dilute solution the activity is equal to the atomic fraction ($a'_S = N'_S = 0.00072$). Then

$$-0.460 = -E = 0.1523 \log \frac{0.00072}{a^{0}_{S}} \qquad (4)$$

The changes in free energy during the transition of a gram atom of sulfur from a more concentrated alloy to a dilute alloy is also calculated from the observed values for the electromotive forces:

$$-\Delta F = 2 \cdot 23060\ E. \qquad (5)$$

The results obtained are set forth in Table 1 and presented in the figure. It is evident from the latter that the isotherm of electromotive forces has 3 portions. At the same time the two receding curves correspond to homogeneous alloys while the horizontal branch corresponds to the stratification interval.

The limits of stratification found by us were to 0.75 and 27.5% S, which is in agreement with the data obtained by other methods. Thus, on the fusibility diagram of the system Fe–S–C they correspond to 0.8 and 29.5% S [7] at 1100°.

TABLE 1

Dependence of the Electromotive Force on the Composition of the alloy at 1250°

Composition of the alloy in % by weight		Atomic fraction N_S	E (mV)	a_S	γ_S	$-\Delta$ (cal/g-at.)
S	C					
0.048	4.4	0.00072	460	0.00072	1.0	21200
0.06	4.4	0.00090	450	0.00084	0.93	20750
0.14	4.2	0.0021	400	0.0018	0.84	18450
0.31	4.0	0.0047	350	0.0039	0.81	16150
0.71	3.3	0.0111	295	0.0087	0.79	13600
29.0	0.2	0.41	190	0.043	0.104	8770
30.0	0.2	0.43	140	0.091	0.287	6460
33.0	0.15	0.46	60	0.306	1.665	2770
35.0	0.15	0.48	0	0.758	1.57	0

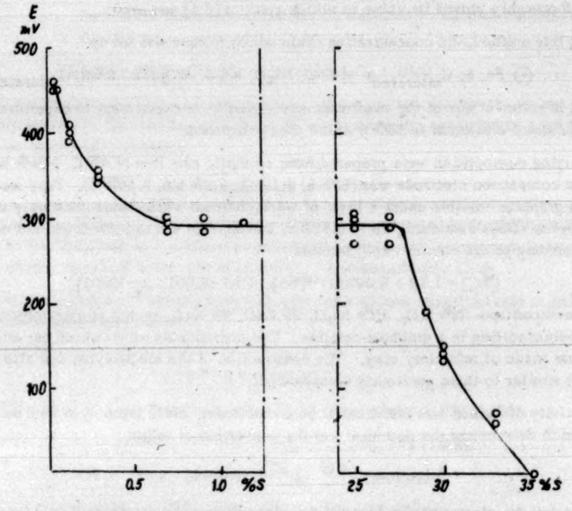

Fig. 1. Dependence of the electromotive force on the content of sulfur in the liquid alloy Fe–S–$C_{saturated}$ at a temperature of 1250°. (The abscissa of the left portion of the curve is on a different scale from that of the right.

It follows from the data of Table 1 that up to the point when stratification begins, the coefficient of activity of sulfur (γ_S) falls with increase in its concentration. Such a course of the changes of γ_S qualitatively coincides with that found by another method for alloys of Fe – FeS at 1600° [1]. However, in our case the fall in the activity coefficient occurs more rapidly (from 1 to 0.79 instead of 0.9). This is due, probably to the lower temperature of our experiments (1250°).

The activity of sulfur (a_S) in alloys compares with its greater content according to the data of Volsky and Agracheva [8]. The latter determined the equilibrium pressure P_{S_2} over solutions of FeS in Fe at a temperature of 1200°.

Taking as standard state an alloy containing 35% S, i.e., placing $a_S^0 = 1$ for it, we find the activity of sulfur from their data according to the equation

$$\log a_S = \frac{1}{2} (\log P_{S_2} - \log P^0_{S_2}). \qquad (6)$$

The activities calculated by this method are compared in Table 2 with those determined from the electromotive forces. The agreement is quite good, particularly if one takes account of the defects of both methods of measurements.

In the last columns of Table 2 the activity coefficients calculated from the formula proposed by Samarin and Shvartsman [9] are presented:

$$\gamma_S' = \frac{1}{1-5\,(N_C + N_S)} \qquad (7)$$

In it N_C and N_S are the atomic fractions of carbon and sulfur. For convenience in comparing them with γ_S coefficients obtained from the electromotive forces, all γ_S' values are divided by 8.7. The data of Table 2 confirm the conclusions of Samarin and Shvartsman [9], that equation (7) can not be applied to alloys containing more than 3% carbon.

TABLE 2

Comparison of a_S and γ_S Calculated from Different Data

Content of S (in %)	a_S*		Content of S (in%)	γ_S** (from the emf)	γ_S'' calculated' according to equation (7)	$\gamma_S = \frac{\gamma_S'}{8.7}$
	Calculated according to equation (6)	According to the emf				
35.0	1	1	0.048	1.0	8.7	1
33.0	0.525	0.404	0.06	0.93	8.78	1.01
30.0	0.144	0.120	0.14	0.84	6.85	0.79
29.0	0.102	0.060	0.30	0.81	6.02	0.69
			0.71	0.79	3.85	0.44

* The standard state alloy contained 35% S, $a_S^0 = 1$.

** The standard state alloy contained 0.048% S and 4.4% C. $\gamma_S^0 = 1$.

SUMMARY

1. Measurements of the electromotive forces of a concentrated element, the electrodes of which consisted of liquid alloys of iron with sulfur, saturated with carbon, were carried out.

2. The activity and activity coefficients of sulfur in these alloys were calculated and the change in free energy in the transition of a gram atom of sulfur from one solution to another was also determined.

3. The results obtained satisfactorily agree with the data found by other methods (fusibility diagram, chemical equilibria).

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[illegible] found. The agreement is quite good, [illegible]

experiments.

In the last columns of Table 4 [illegible] and [illegible] are presented.

[illegible] and N_S are the atomic fractions of sulfur and iron [illegible]

TABLE 4

Comparison of a_{Fe} and γ_S Calculated from [illegible]

[illegible]	[illegible]	[illegible]	[illegible]	a_{Fe}	Calculated according to equation (4)	Content of S
1	[illegible]	1.0	[illegible]	1	1	50.0
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.565	49.5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.144	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.125	[illegible]

[illegible] standard state [illegible]

[illegible]

SUMMARY

1. Measurements of the electromotive force of a concentration element [illegible] of liquid alloys of iron with sulfur [illegible] were carried out.

2. The activity and activity coefficients of [illegible]

3. The results obtained satisfactorily agree with [illegible]

LITERATURE CITED

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

(5) [illegible]

(6) [illegible]

(7) [illegible]

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(9) [illegible]

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CALCULATION OF THE VISCOSITY OF BINARY SYSTEMS. I

R. P. Airapetova and R. I. Filatova

In the works of Panchenkov [1,2] a formula for the dependence of viscosity of liquids on the temperature is introduced. The author indicates that this formula can be used for finding the dependence of the viscosity of mixtures on the composition. The formula of Panchenkov has been verified for a large number of liquids, and also for 5 binary systems [1,3].

We have collected much experimental material on the viscosity of binary systems. It was of interest to investigate how the calculated values for the viscosity would agree with our experimental data.

In the calculations of the viscosity of pure components and their mixtures we used the somewhat modified Panchenkov formula [1]:

$$\eta = 4 A \rho^{4/3} T^{1/2} \operatorname{Sh}^2 \frac{E}{2RT},$$

which is more convenient in the calculations.

In the present article the calculated values for the viscosity of the system dichloroethane – methyl alcohol (Table 1), dichloroethane – ethyl alcohol (Table 2), dichloroethane – propyl alcohol (Table 3), dichloroethane – butyl alcohol (Table 4) and dichloroethane – isoamyl alcohol (Table 5) are presented.

The experimental data on the viscosity and density of the systems enumerated [illegible] been published [illegible]

In Tables 1-5, along with the calculated values for the viscosity, the percentage deviations of the calculated viscosity value from the experimental value ($\Delta\eta\%$), the value of the bond energy of a molecule of the mixture (E_c) and the logarithm of the constant A_s, as a function of the composition of the mixture, are given.

For calculating the values of log A_s we used the experimental data for the viscosity at 60° [4], and consequently the calculated values for the viscosity at this temperature are not presented in Tables 1-5.

It is evident from the data of Table 1.5 that the calculated values for the viscosity are in excellent agreement with the experimental data. The average deviation of the experimental from the calculated values for the viscosity is only in excess of 1% in a few cases.

It is of interest to note that the functional dependence between the bond energy of the molecules of the mixture and the composition of the mixture can be used to construct a physico-chemical analytical composition-property diagram. The dependence of the bond energy of the molecules on the composition in the system methyl alcohol-dichloroethane (Table 1) is expressed by a curve which passes through a maximum (Fig. 1). The components of this system react chemically [4], which leads to an increase in the bond energy of the molecules and the appearance of a maximum on the curve.

In Figure 2, the "bond energy – composition" curves of the system ethyl alcohol – dichloroethane (curve I), propyl alcohol – dichloroethane (curve II), butyl alcohol – dichloroethane (curve III) and isoamyl alcohol – dichloroethane (curve IV) are presented in the form of a single diagram. The components of these systems do not react chemically [4]. The "bond energy – composition" curves are convex toward the abscissa axis and the convexity increases from the system ethyl alcohol – dichloroethane to the system isoamyl alcohol – dichloroethane. The extent of association of the alcohols diminishes in the same sequence.

SUMMARY

1. Viscosity calculations for five binary systems were carried out according to Panchenkov's formula. Excellent agreement was obtained between the calculated values for viscosity and the experimental data.

TABLE 1

The System Methyl Alcohol – Dichloroethane

CH_3OH (moles %)	Viscosity, calculated according to Panchenkov's formula						E_{12} = 2851,3	
	30°		40°		50°		E_C	log A_s
	$\eta \cdot 10^3$	$\Delta\eta$, %	$\eta \cdot 10^3$	$\Delta\eta$, %	$\eta \cdot 10^3$	$\Delta\eta$, %		
0.00	7,249	−0.10	6.423	+0.63	5.716	−0.14	2197.0	$\bar{6}$ 93338
15.68	6.732	+ 2.23	5.895	+2.13	5.217	+ 0.93	2378.8	$\bar{6}$.78193
23.69	6.503	+ 1,46	5.672	+1.36	4.999	+ 0.18	2453.7	$\bar{6}$.72257
42.17	6.239	+ 1.86	5.395	+1.45	4.741	+ 0.68	2579.9	$\bar{6}$.64227
53.74	6,014	−0.30	5.211	−0.31	4.548	−0.74	2625.6	$\bar{6}$.61585
62.21	5,974	+ 0.64	5.146	+1.02	4.297	−0.02	2643.0	$\bar{6}$.61943
69.06	5.821	−0.05	5.044	+0.78	4.389	−0.75	2647.0	$\bar{6}$.62697
79.82	5.665	−0.54	4.920	+0.10	4.285	−0.88	2635.5	$\bar{6}$.66023
83.93	5.639	+ 0.39	4.888	+0.74	4.272	+ 0.40	2625.2	$\bar{6}$.68225
91.20	5.513	+ 0.46	4.777	+0.32	4.190	−0.21	2599.2	$\bar{6}$.72558
100.00	5.228	−0.02	4.538	−0.02	3.990	−0.84	2554.3	$\bar{6}$.78714

TABLE 2

The System Ethyl Alcohol – Dichloroethane

C_2H_5OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E_{12} = 2683.7	
	30°		40°		50°		E_C	log A_s
	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %		
0.00	7.240	−0.10	6.423	+0.63	5.716	−0.14	2197.0	$\bar{6}$.93338
6.40	7.097	+ 2.09	6.251	+2.04	5.559	+ 0.54	2260.6	$\bar{6}$.88641
12.15	6.870	+ 1.34	6.034	+1.61	5.354	+ 0.33	2319.8	$\bar{6}$.83797
22.95	6.699	+ 0.23	5.834	+0.81	5.137	+ 0.26	2436.7	$\bar{6}$.75712
32.79	6.673	+ 0.07	5.795	+0.48	5.102	−0.25	2550.5	$\bar{6}$.69244
39.12	6.724	+ 0.33	5.817	+0.19	5.086	−0.33	2625.3	$\bar{6}$.65371
47.26	6.865	−0.12	5.865	−0.51	5.153	−0.15	2726.3	$\bar{6}$.60672
59.89	7.239	−0.17	6.192	+0.23	5.339	−0.39	2891.2	$\bar{6}$.54081
75.20	7.883	−0.31	6.679	+0.12	5.694	−0.51	3104.5	$\bar{6}$.46804
88.19	8.644	−0.02	7.360	−0.23	6.227	−0.84	3295.8	$\bar{6}$.44623
100.00	9.849	+ 0.07	8.187	+0.27	6.881	−0.58	3480.8	$\bar{6}$.38680

TABLE 3

The System Propyl Alcohol – Dichloroethane

C_3H_7OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E_{12} = 2771.0	
	30°		40°		50°		E_C	log A_s
	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %		
0.00	7.249	−0.10	6.423	+0.63	5.716	−0.14	2197.0	$\bar{6}$.93338
11.82	7,049	+ 1.14	6.175	+1.41	5.469	−0.25	2347.8	$\bar{6}$.83115
21.63	7.153	+ 3.84	6.237	+1.23	5.461	−0.49	2496.3	$\bar{6}$.74809
32.60	7.392	+ 1.77	6.385	+1.46	5.566	+ 0.43	2687.7	$\bar{6}$.63714
55.79	8.984	−0.26	7.578	+0.20	6.465	−0.29	3176.3	$\bar{6}$.42860
67.20	10.324	−0.15	8.579	+0.76	7.195	−0.21	3460.2	$\bar{6}$.31234
83.60	13.226	−0.41	10.737	+0.24	8.857	−0.17	3917.5	$\bar{6}$.13535
100.00	17.685	+ 0.03	14.015	+1.13	11.277	−0.02	4433.5	$\bar{7}$.94092

2. A "bond energy – composition" diagram was constructed. The presence of a maximum on the "bond energy–composition" curve is evidence of chemical reaction of the components. "Bond energy – composition" curves which were convex toward the absciss[illegible]is indicate the absence of reaction of the components.

TABLE 4

The System n-Butyl Alcohol— Dichloroethane

C_4H_9OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E_{12} = 3030.8	
	30°		40°		50°			
	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$, %	E_C	log A_s
0,00	7.249	−0.10	6.423	+0.63	5.716	−0.14	2197.0	$\bar{6}$.93338
9.69	7.255	+ 1,60	6.331	+2.13	5,600	+ 0.29	2366.3	$\bar{6}$,82761
20.52	7,507	+ 0.78	6.521	+1.50	5.707	−0.05	2569,3	$\bar{6}$,72109
31.78	8,150	+ 0,85	7,014	+1.36	6,074	+ 0.21	2809,8	$\bar{6}$.60610
46.83	9.409	−0.10	7.955	+0.80	6.743	−0.71	3157,8	$\bar{6}$.45067
56,18	10.568	−0.46	8.824	+1.03	7.449	+ 0.03	3392.7	$\bar{6}$.35333
67,68	12,800	+ 0.66	10.522	+1.56	8.784	+ 0.84	3701.9	$\bar{6}$.24085
85,60	17.408	−0.18	13.935	+1.09	11.325	+ 0.86	4225,5	$\bar{6}$,04099
100,00	22,586	+ 0,17	17.634	+0.26	13.987	−0.45	4685.0	$\bar{7}$.86885

TABLE 5

The system Isoamyl Alcohol —Dichloroethane

iso-$C_5H_{11}OH$ (in moles %)	Viscosity, calculated according to Panchenkov's formula						E_{12} = 3021.0	
	30°		40°		50°			
	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %	$\eta \cdot 10^3$	$\Delta\eta$ %	E_C	log A_s
0.00	7.249	−0.10	6.423	+0.63	5.716	−0,14	2197.0	$\bar{6}$.93338
12.72	7.510	+ 1.07	6.578	+1.57	5.825	+ 0.67	2453.5	$\bar{6}$.79261
22.01	7,954	−0.20	6.903	+0.55	6.034	+ 0.07	2640.1	$\bar{5}$.70503
32.69	9.150	+ 1.06	7.819	+2.22	6.749	+ 1.48	2913.1	$\bar{6}$.59189
43.02	10.275	−0.11	8.669	+1.04	7.384	+ 0.26	3213.3	$\bar{6}$.45055
57.65	13,000	+ 0.12	10.704	+0.53	8.923	+ 0.06	3699.2	$\bar{6}$.23624
66.39	15.435	+ 0.74	12.492	+1.58	10.242	+ 0.96	4023.0	$\bar{6}$.09717
80.49	20.960	+ 0.73	16.417	+1.39	13.082	−0.07	4599.2	$\bar{7}$.84506
88.80	25.046	−0.21	19.288	+0.99	15.083	+ 0.07	4969.8	$\bar{7}$.67478
100.00	32.665	−0.02	24.465	+0.71	18.650	−0.08	5505.5	$\bar{7}$.42849

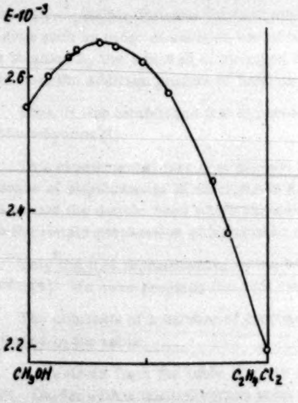

Fig. 1. Dependence of the bond energy of the molecules on the composition in the system methyl alcohol-dichloroethane.

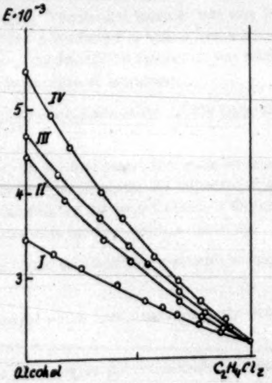

Fig. 2. "Bond energy — composition" curves of the systems: I) Ethyl alcohol – dichloroethane; II) propyl alcohol – dichloroethane; III) butyl alcohol – dichloroethane IV) isoamyl alcohol – dichloroethane.

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INVESTIGATION IN THE FIELD OF CONJUGATED SYSTEMS

LIV. THE ORDER OF ADDITION OF HYPOBROMOUS ACID TO VINYLALKYLACETYLENES. SYNTHESIS AND PROPERTIES OF α-OXIDES OF VINYLACETYLENES

A. A. Petrov

It was shown in the preceding articles that bromine [1] and alkylhypohalogenites [2] add to vinylalkylacetylenes at the double bond. The triple bond practically does not enter into the reaction and 1,4-addition does not occur. The substances obtained were used for the synthesis of enyne halogen derivatives, acetylenic ketones and their enolic ethers.

It can be assumed that the same order of addition will be observed in the addition to vinylalkylacetylenes of hypohalogen acids. With the object of establishing the order of addition of hypobromous acid to vinylalkylacetylenes we investigated the reaction of vinylmethyl- and vinylethylacetylene with an aqueous solution of bromoacetamide [3].

Vinylalkylacetylenes can add HOBr with the formation of six substances: three of these are alcohols and three ketones.

$$R-C\equiv C-CH(OH)-CH_2Br \qquad (I)$$

$$R-C\equiv C-CHBr-CH_2OH \qquad (II)$$

$$R-CBr=C(OH)-CH=CH_2 \longrightarrow R-CHBr-CO-CH=CH_2 \quad (III)$$

$$R-C(OH)=CBr-CH=CH_2 \longrightarrow R-CO-CHBr-CH=CH_2 \quad (IV),$$

$$R-CBr=C=CH-CH_2OH \quad (V)$$

$$R-C(OH)=C=CH-CH_2Br \longrightarrow R-CO-CH=CH-CH_2Br \quad (VI).$$

The addition products of HOBr actually obtained boiled in a narrow temperature range and had the following chemical properties.

1. They yielded acetates as a result of the action of acetic anhydride. Thus, they consisted of alcohols and not of ketones and, consequently, formulas (III), (IV) and (VI) are excluded.

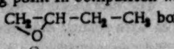
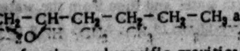
2. Upon distillation over KOH they yielded α-oxides of vinylalkylacetylenes. This conversion forces us to reject all the possible formulas for the bromohydrins except (I) and (II). The second formula was very slightly probable, since such an order of addition has never been observed for HOBr. A bromohydrin with a formula similar to (II) was obtained by the addition of hydrogen bromide to the α-oxide of vinylmethylacetylene. It was markedly different from the addition product of HOBr to vinylmethylacetylene in its index of refraction.

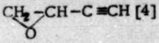
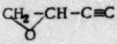
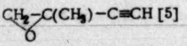
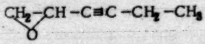
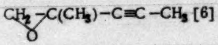
Thus, it was established that hypobromous acid adds to vinylalkylacetylene at the double bond with formation of the bromohydrins (I).

This experimental fact is of interest from two points of view. In the first place, it is once more evidence of the presence of displacement of electrons in the molecules of vinylalkylacetylenes under the influence of alkyl radicals toward the double bond which consequently becomes more reactive. In the second place, it discloses the route to the simple preparation of acetylenic oxides which have hitherto been hard-to-obtain substances.

Only the first representative of the homologous series of acetylenic oxides of this type with normal structure was known [4]. We have prepared the next two homologs.

The constants of a number of previously known acetylenic oxides which were described in the present work are presented in the table.

It is evident from the table that the character of substitution in this oxide series markedly influences the constants. Oxides with a normal carbon atom chain have a considerably higher boiling point in comparison with isomers with a branched structure and with their normal saturated analogs (the oxide  $CH_2-CH-CH_2-CH_3$ (O bridging CH_2 and CH) boils at 58.5-59° [7], the oxide  $CH_2-CH-CH_2-CH_2-CH_2-CH_3$ at 123-124° [8]. They also differ in the considerably greater indexes of refraction and specific gravities. The values of the molecular refraction found for them exceed the calculated values to a greater extent than in the case of unsubstituted oxides and oxides with a branched structure.

Substance	Boiling point	d_4^{20}	n_D^{20}	MR_D	
				Found	Calculated
 $CH_2-CH-C\equiv CH$ [4]	86–87°	0.945 (23°)	1.427	18.50	18.11
 $CH_2-CH-C\equiv C-CH_3$	125.5–126.6	0.9499	1.4542	23.41	22.73
 $CH_2-C(CH_3)-C\equiv CH$ [5]	91–91.5	0.8939 (18°)	1.4205	23.27	22.73
 $CH_2-CH-C\equiv C-CH_2-CH_3$	142–143	0.9182	1.4530	28.30	27.35
 $CH_2-C(CH_3)-C\equiv C-CH_3$ [6]	40–41 (22 mm)	0.9264 (9°)	1.4461	27.70	27.60

Of the chemical properties of the oxides obtained by us we investigated the addition of water, methyl alcohol and hydrogen bromide to methylacetylenylethyleneoxide.

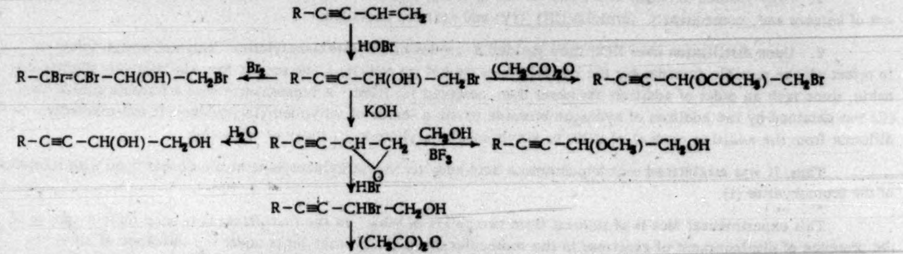
The addition of water proceeds very readily – upon heating for 3 hours to 100°.

According to the literature data acetylenylethylene oxide requires heating at that same temperature for 20 hours for conversion into the glycol [4]. The glycol thereby formed is a crystalline substance with a higher melting point (56-57°) than that of the unsubstituted glycol (39.5-40.5°) [4].

In exactly the same way the reaction of the oxide under investigation with methyl alcohol in the presence of the etherate of boron fluoride proceeds very readily. In accordance with the previously established rule of addition of alcohols to unsaturated oxides in the presence of BF_3 [9], which was confirmed for acetylenic oxides by Perveev [10], the glycol ether obtained was assigned the structure of a primary alcohol.

As a result of the addition to the same oxide of hydrogen bromide, a bromohydrin was obtained which was isomeric with that formed by the action of HOBr on vinyl-methylacetylene [11]. In comparison with the latter it was considerably more readily acetylated, which was an extra indication of the primary character of the hydroxyl group.

The conversions described in the present article are presented in the following scheme:



EXPERIMENTAL

1. Preparation and Properties of the Bromohydrins

Vinylmethylacetylene (90 g, a double excess) was shaken for a duration of 30 minutes with bromoacetamide acidified with H_2SO_4 which contained 0.72 moles of this substance in 1 liter. The bromoacetamide solution was preliminarily cooled until considerable quantities of ice formed.

The bromohydrin was extracted with ether from the aqueous solution (after its filtration through cotton and saturation with sodium chloride). The bromohydrin was extracted from the oil (after distilling off the excess hydrocarbon and concentrating to a small volume) initially with water and then from the water with ether. The quantity of insoluble products (bromides, probably) proved to be negligible (4 g). About 6.5 g of the bromohydrin dissolved in 100 ml of water.

Upon vacuum distillation the substance almost entriely passed over at a constant temperature. The yield of pure substance amounted to about 82 g (70%). The residue from the distillation was 6 g (a resinified mass).

B. p. 89.5° at 10 mm, 103-103.5° at 20 mm; d_4^{20} 1.5124; n_D^{20} 1.5172; MR_D 32.62. C_5H_7OBr $\vDash$. Calculated 32.48.

0.1420 g sub.: 0.1634 g AgBr. 0.1348 g sub.; 13.28 g benzene: Δt 0.315°. Found %: Br 48.97. M 163.2. C_5H_7OBr. Calculated % : Br 49.03. M 163.0.

The bromohydrin of vinylethylacetylene was obtained in a yield of 40% by the same method.

B. p. 96.5-97° at 10 mm; 108-108.5° at 20 mm; d_4^{20} 1.4071; n_D^{20} 1.5070; MR_D 37.45. C_6H_9OBr $\vDash$. Calculated 37.20.

0.1268 g sub.: 0.1346 g AgBr. Found % : Br 45.17. C_6H_9OBr. Calculated % : Br 45.14.

Both bromohydrins were converted into the acetates (yield 85%) by the action of a 50% excess of acetic anhydride and 1 drop of H_2SO_4.

The following constants were found for the acetate of the bromohydrin of vinylmethylacetylene:

B. p. 98° at 10 mm; 112.5-113° at 20 mm; d_4^{20} 1.3970; n_D^{20} 1.4864; MR_D 42.17. $C_7H_9O_2Br$ $\vDash$. Calculated 41.84.

0.1656 g sub.: 0.1527 g AgBr. Found % : Br 39.24. $C_7H_9O_2Br$. Calculated % : Br 39.06.

The following constants were found for the acetate of the bromohydrin of vinylethylacetylene:

B.p. 104.5-105° at 10 mm; d_4^{20} 1.3267; n_D^{20} 1.4820; MR_D 47.08. $C_8H_{11}O_2Br$ $\vDash$. Calculated 46.56.

0.1428 g sub.: 0.1238 g AgBr. Found % : Br 36.89. $C_8H_{11}O_2Br$. Calculated % : Br 36.48.

1,3,4-Tribromopenten-3-ol-2 was obtained in a yield of 88% by the action of the calculated quantity of bromine in chloroform on the bromohydrin of vinylmethylacetylene.

B.p. 135.5° at 8 mm; 139.5° at 10 mm; d_4^{20} 2.2090; n_D^{20} 1.5918; MR_D 49.44. $C_5H_7OBr_3$. Calculated 50.31.

0.1744 g sub.: 0.3046 g AgBr. Found % : Br 74.32. $C_5H_7OBr_3$. Calculated % : Br 74.26.

2. Preparation and Properties of the Oxides of Vinylalkylacetylenes

The oxides of vinylalkylacetylenes were prepared by distilling the bromohydrins or their acetates over concentrated KOH. The substances were introduced in the form of drops into the heated alkali while the distillate was being continuously distilled off. The yield of oxides amounted to around 85%. The constants are given in the table.

The following constants were found for the oxide of vinylmethylacetylene:

0.1663 g sub.: 0.4467 g CO_2; 0.1163 g H_2O. Found % : C 73.30; H 7.86; C_5H_6O. Calculated % : C 73.14; H 7.37.

The following constants were found for the oxide of vinylethylacetylene:

0.1810 g sub.: 0.4956 g CO_2; 0.1365 g H_2O. Found % : C 74.72; H 8.44. C_6H_8O. Calculated % : C74.96; H 8.39.

The glycol was obtained by heating the oxide of vinylmethylacetylene with a 5-fold quantity of water in a sealed glass tube at 100° for 3 hours. The latter was separated from water by salting it out with potash, was dissolved in ether, and the ethereal solution was dried with roasted potash. The yield of glycol amounted to 60%.

M.p. 56-57° (from benzene) b.p. 111.5-112.5° at 8 mm.

0.1606 g sub.: 0.3531 g CO_2; 0.1163 g H_2O. Found % : C 60.01; H 8.10. $C_5H_8O_2$. Calculated % : C 59.98; H 8.06

The glycol consisted of colorless crystals, quite soluble in alcohol and ether, more poorly soluble in chloroform and difficultly soluble in cold benzene.

Evolution of heat was observed during the action on a solution of 6 g of the oxide in 50 ml of methyl alcohol of 1 drop of the etherate of boron fluoride. After standing for 5 hours the liquid was neutralized with solid KOH and subjected to distillation, initially at ordinary pressure and then in a vacuum. The yield of the monoether of the glycol amounted to 6 g (72%).

B.p. 72.5° at 10 mm; 84-84.5° at 20 mm; d_4^{20} 0.9925; n_D^{20} 1.4572; MR_D 31.33. $C_6H_{10}O_2$ $\models$. Calculated 31.07.

0.1623 g sub.: 0.3773 g CO_2; 0.1307 g H_2O. 0.0778 g sub.: 0.1606 g AgI (according to Zeisel's method). Found %: C 63.44; H 9.01; OCH_3 27.28. $C_6H_{10}O_2$. Calculated % : C 63.13; H 8.83; OCH_3 27.13.

By the careful addition of the oxide to concentrated hydrobromic acid a bromohydrin was obtained in a yield of about 70% which was isomeric with that obtained from the hydrocarbon.

B.p. 88.5-89° at 10 mm; 102-103° at 20 mm; d_4^{20} 1.5120; n_D^{20} 1.5312; MR_D 33.37. C_3H_7OBr. Calculated 32.46.

0.1418 g sub.: 0.1641 g AgBr. Found % : Br 49.25. C_5H_7OBr. Calculated % : Br 49.03.

When a solution of this bromohydrin in acetic anhydride was let stand, a reaction, notable for the evolution of heat, began without the addition of acid.

The acetate of this bromohydrin had the following properties:

B.p. 97-97.5° at 10 mm; 111.5-112° at 20 mm; d_4^{20} 1.3956; n_D^{20} 1.4938; MR_D 42.76. $C_7H_9O_2Br$ $\models$. Calculated 41.84.

0.1610 g sub.: 0.1484 g AgBr. Found % : Br 39.22. $C_7H_9O_2Br$. Calculated % : Br 39.06.

The oxide of vinylmethylacetylene, described above, was obtained by distilling this bromohydrin or its acetate over KOH.

SUMMARY

1. The order of addition of hypobromous acid to vinylmethyl- and vinylethyl-acetylenes was investigated. It was established that the addition proceeds at the ethylenic bond. The corresponding bromohydrins, their acetates and the bromide were isolated and characterized.

2. The oxides of vinylmethyl- and vinylethylacetylenes were obtained for the first time by the action of caustic alkali on the bromohydrins. The hydration of the first oxide and the addition of methyl alcohol and of hydrogen bromide were investigated.

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* See Consultants Bureau Translation, p. 1973

** See Consultants Bureau Translation, p. 1299

*** See Consultants Bureau Translation, pp. 1623, 2013

**** See Consultants Bureau Translation, p. 1757

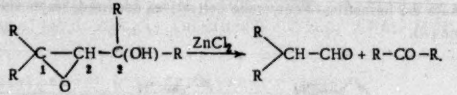
INVESTIGATIONS IN THE FIELD OF ALCOHOL OXIDES (OXIDOLS)

IV. PROPERTIES OF THE α-OXIDES OF ALLYL AND PROPENYL DERIVATIVES OF PHENOL AND o-CRESOL

V. I. Pansevich-Kolyada and Z. B. Idelchik

The unique properties of α,β-alcohol oxides, which are doubtless due to the presence in their structure of two functional groups bound to neighboring carbon atoms, were established by the preceding investigations [1,2,3] of these compounds. It was also shown that the behavior of the oxide ring of these substances in chemical reactions is to a considerable extent dependent on the radicals adjacent to the oxide carbon atoms.

A general property of all the oxidols investigated by us appears to be their acetylation at the hydroxyl group upon heating with acetic anhydride and the formation of oxidoacetates due to the preservation of the oxide ring. A certain difference between the oxidols of the aliphatic series and those with aromatic radicals is observed in the reaction with anhydrous zinc chloride. Upon heating with fused zinc chloride, oxidols of the fatty series are cleaved at the bond between carbon atoms 2 and 3 with formation of aldehydes and ketones:



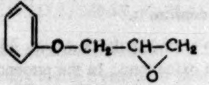
An oxidol with a phenyl radical at the tertiary alcoholic group, 2-methyl-4-phenyloxido-2,3-pentanol-4 [1] proves to be very unstable and is cleaved into acetophenone and isobutyraldehyde upon being kept in a desiccator over H_2SO_4, P_2O_5 or $CaCl_2$ at room temperature. The oxidol 2-methyl-4-benzyloxido-2,3-pentanol-4 [3], in which the phenyl radical is separated from the tertiary alcoholic group by a CH_2 group, is isomerized into the unsaturated glycol 2-methyl-4-benzylpenten-2-diol-3,4 by the action of zinc chloride and dilute sulfuric acid, while on heating with an aqueous solution of ammonia it yielded the aminodiol 2-methyl-4-benzyl-3-aminopentadiol-2,4.

It was established that 2-methyl-4-benzyloxido-2,3-pentanol-4 and the unsaturated glycol are capable of mutual interconversion which proceeds with disruption and reduction of the oxide ring. These conversions appear to be a hitherto unobserved form of tautomerism which we call oxidoenolic tautomerism.

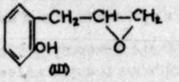
In the present work the study of α-oxides of allyl and propenyl derivatives of phenol and o-cresol is carried out; it turned out in the course of this work that the properties of the oxide ring of these compounds are no less interesting and unique than those of the previously studied oxidols, and are determined to a considerable extent by the distance of the oxide ring from the benzene ring.

We synthesized the allyl ethers of phenol and o-cresol by the Claisen reaction [4,9]; o-allylphenol and o-allyl-o-cresol were obtained via the rearrangement of these ethers. o-Propenylphenol and o-propenyl-o-cresol were obtained by the isomerization of o-allylphenol and o-allyl-o-cresol.

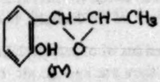
The allyl and propenyl derivatives of phenol and o-cresol were oxidized by peroxyacetic acid and for all, except the allyl ether of o-cresol, the corresponding oxides were obtained:



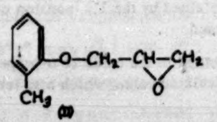
(I)



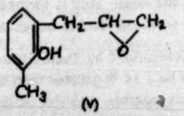
(III)



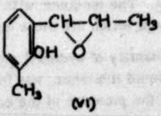
(IV)



(II)



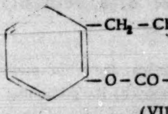
(V)



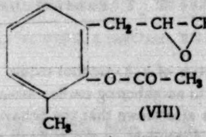
(VI)

The oxide of the allyl ether of o-cresol (II) proved to be a very unstable compound and on vacuum distillation was almost entirely split with recovery of o-cresol, while only an insignificant portion of the substance had data close to those calculated for the oxide of the allyl ether of o-cresol.

Upon boiling the oxides of o-allylphenol (III) and o-allyl-o-cresol (V) with acetic anhydride, acetylation, similar to that previously studied for alcohol oxides [2,3], proceeded at the phenolic hydroxyl group with retention of the oxide ring; the oxidoacetates (VII) and (VIII) were thereby obtained:



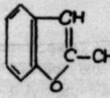
(VII)



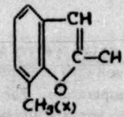
(VIII)

a-Oxides are isomerized under the action of zinc chloride, as is well known [5], depending on the location of the oxide ring in the aldehyde or ketone. The behavior toward this reagent of *a*,*β*-alcohol oxides is identical, as indicated above, and depends on the radicals adjacent to the oxide carbon atoms. In contrast to these substances, the oxide of o-allylphenol (III) remains unchanged on heating with anhydrous zinc chloride.

The oxides of o-propenylphenol (IV) and o-propenyl-o-cresol (VI) are quite different from all the oxidols previously studied by us. These substances are not appreciably changed in air; however when kept in a desiccator over sulfuric acid at room temperature the formation of cumarone derivatives occurred, respectively: 2-methylcumarone (IX) and 2,7-dimethylcumarone (X):

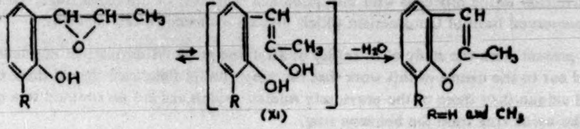


(IX)



(X)

The formation of cumarone derivatives from the oxidophenols (IV) and (VI) is possible only via the preliminary conversion of the oxidophenols into the unsaturated phenoloalcohols (XI) which, eliminate a molecule of water similarly to the 1,4-glycols [7], and yield cumarone derivatives :



On boiling the oxide of o-propenyl-o-cresol (VI) with acetic anhydride, dehydration and formation of 2,7-dimethylcumarone (X) also occurred. It is necessary to assume that the behavior of the oxide of o-propenylphenol (IV) with acetic anhydride will be the same, but on account of the absence of the substance we cannot establish this.

The conversion of the oxidophenols (IV) and (VI) into the cumarone derivatives (IX) and (X) can be explained by the presence of oxidoenolic tautomerism [3] and in its turn serves to confirm it.

The oxides of o-propenylphenol (IV) and o-propenyl-o-cresol (VI) are in equilibrium with their enolic form (XI). When they are kept in air, the equilibrium is displaced toward the oxido form. In the presence of dehydrating substances the equilibrium is displaced toward the enol form due to the consumption of the enol in the formation of a furan ring. The readiness with which the furan ring is formed is explained by the 1,4-position of the enolic hydroxylic groups which are close together when the double bonds are formed.

The quantity of hydroxyl groups, determined by Tserevitinov's method in the oxide of o-propenyl-o-cresol, which is a liquid substance, was found to be 1.14 % greater than the calculated value, which also serves as a confirmation of the presence of the enol form together with the oxide.

Thus, the properties of the *a*-oxides of allyl and propenyl derivatives of phenols are identical and also differ from the properties of *a*,*β*-alcohol oxides. In allylphenol oxides the oxide ring is passive and remains unchanged by the action not only of acetic anhydride, but also of zinc chloride. The oxide ring of the oxides of the o-propenylphenols is very stable due to the presence in it of the phenyl radical and the oxides of o-propenylphenols are capable of being converted into their unsaturated tautomeric enols with a hydroxyl group at the double bond. Under suitable conditions the enols formed readily eliminate a molecule of water, due to the hydroxyl groups of the enol and phenol and yield cumarone derivatives.

EXPERIMENTAL

Oxidation of the Allyl Ether of Phenol with Peroxyacetic Acid

The allyl ether of phenol was prepared by heating a mixture of phenol with allyl bromide and anhydrous potash in acetone [4].

B.p. 82° (10 mm); n_D^{20} 1.5193; d_4^{20} 0.9796; MR_D 41.54; Calculated 41.35.

15.5 g of 73% peroxyacetic acid was slowly added to 20 g of allyl ether in 40 ml of dry ether. The oxidation proceeded slowly without evolution of heat or change in the color of the reaction mixture. After 22 days all the peroxyacetic acid had reacted and consequently the acetic acid was neturalized with soda, the reaction products were extracted with ether, dried with $MgSO_4$ and vacuum distilled. 6 g of substance (I) with a b.p. of 101-105° (4.5 mm) was isolated. This was a mobile yellow colored liquid with the odor of tobacco.

n_D^{20} 1.5311; d_4^{20} 1.1145; MR_D 41.63; Calculated 40.68.

0.2456 g sub.: 0.6453 g CO_2; 0.1513 g H_2O. 0.1496, 0.2889 g sub.: 21.08 g benzene: Δt 0.254, 0.462°. Found %: C 72.10; H 6.89; M 143.4, 147.7. $C_9H_{10}O_2$. Calculated %: C 72.0; H 6.66; M 150. It contained no active hydrogen.

Oxidation of o-Allylphenol with Peroxyacetic Acid

o-Allylphenol was prepared by boiling the allyl ether of phenol in a stream of carbon dioxide [4].

B.p. 97-98° (8 mm); n_D^{20} 1.5440; d_4^{20} 1.0210; MR_D 41.48; calculated 41.22. Found %: OH 12.27. Calculated %: OH 12.68.

26 g of 93% peroxyacetic acid was slowly added to 42 g of o-allylphenol in 84 ml of dry ether. The oxidation proceeded with evolution of heat; the temperature of the mixture was maintained at 20-25°. The color of the reacting substances became orange. After 3 days the peroxyacetic acid had reacted. The oxidation products were treated, as indicated above, dried with $MgSO_4$ and vacuum distilled. 19.3 g of substance (III) with a b.p. of 154° (15 mm) was obtained. It was a mobile, odorless, light orange liquid which contained active hydrogen.

n_D^{20} 1.5558; d_4^{20} 1.1795; MR_D 40.88; calculated 40.56.

0.2245 g sub.: 0.5892 g CO_2; 0.1358 g H_2O. 0.2473 g sub.; 37.92 ml CH_4 (0°, 760 mm). 0.1486 g sub.; 16.11 g benzene; Δt 0.312°. Found %: C 71.6; H 6.83; OH 11.71; M 151.9. $C_9H_{10}O_2$. Calculated %: C 72.00; H 6.66; OH 11.33; M 150.

Reaction of the Oxide of o-Allylphenol with Acetic Anhydride

2 g of the oxide was boiled for 4 hours with 10 g of acetic anhydride. The acetic anhydride was eliminated and the reaction products were vacuum distilled. 1.5 g of a colorless mobile liquid (VII) with a sharp odor was isolated.

B.p. 142-143° (8 mm); n_D^{20} 1.5220; d_4^{20} 1.1550; MR_D 50.71; calculated 49.92.

0.1988 g sub.: 0.5003 g CO_2; 0.1128 g H_2O. 0.0965, 0.2124 g sub.: 17.19 g benzene. Δt 0.159, 0.352°. Found %: C 68.63; H 6.3; M 181.5; 180.42. $C_{11}H_{12}O_3$. Calculated %: C 68.75; H 6.25; M 192. (Active hydrogen was absent).

The Action of Zinc Chloride on the Oxide of o-Allylphenol

1.5 g of finely divided anhydrous zinc chloride was added to 5.5 g of oxidophenol in 25 ml of dry ether and the mixture was heated for 1.5 hours on a boiling water bath. After eliminating the ether the substance was vacuum distilled. 3 g of substance was obtained; the carbonyl group was absent.

B.p. 133.5° (7 mm); n_D^{20} 1.5580; d_4^{20} 1.1780; MR_D 40.37; calculated 40.56.

The oxide of o-allylphenol was recovered without change.

Oxidation of o-Propenylphenol with Peroxyacetic Acid

o-Propenylphenol was prepared by isomerizing o-allylphenol [6].

B.p. 154° (21 mm); m.p. 33-34°. Found %: C 80.78; H 7.68. Calculated %: C 80.6; H 7.49.

17.8 g of 73% peroxyacetic acid was slowly added to 23 g of o-propenylphenol, dissolved in 46 ml of dry ether. The oxidation proceeded with evolution of heat; the temperature was maintained at 20-25°. The contents of the flask acquired an orange color toward the end of the oxidation. After two days there was no peroxide present. The products of the reaction were treated, as indicated above, with dried $MgSO_4$ and, after distilling off the ether, were vacuum distilled. 15 g of a substance was obtained which boiled at 147-148° (10 mm). After some time the substance crystallized as white needles, readily soluble in ether, alcohol, chloroform, and benzene, and poorly soluble in petroleum ether. They were recrystallized from the latter and 14 g of coarse flakes with a m.p. of 58-59° was obtained. The substance (IV) contained active hydrogen.

0.1158 g sub.: 0.3054 g CO_2; 0.0696 g H_2O. 0.0893 g sub.: 15.02 ml CH_4 (22°, 746 mm). 0.1479 g sub.; 17.89 g benzene: Δt 0.273°. Found %: C 71.92; H 6.75; OH 11.32; M 155.6. $C_9H_{10}O_2$. Calculated %: C 72.0; H 6.66; OH 11.3; M 150.

Upon keeping this crystalline substance in a desiccator over sulfuric acid overnight an oily, dirty-yellow colored liquid with the odor of toluene was formed. By fractionally distilling the liquid, substance (IX) with a b.p. of 76-77° (8 mm) was formed which did not contain active hydrogen.

n_D^{20} 1.5580; d_4^{20} 1.0581; MR_D 39.31; calculated 39.34.

0.1540 g sub.: 0.4635 g CO_2; 0.0844 g H_2O. 0.0894, 0.1955 g sub.: 1974 g benzene: Δt 0.186, 0.399°. Found %: C 82.08; H 6.13; M 125.2, 127.8. C_9H_8O. Calculated %: C 81.80; H 6.60; M 132.

From the substance with b.p. 76-77° (8 mm) a picrate was formed which melted at 74-79° and was cleaved in a desiccator over sulfuric acid into picric acid and methylcumarone; this is in agreement with the literature data for methylcumarone picrate [8].

Oxidation of the Allyl Ether of o-Cresol with Peroxyacetic Acid

The allyl ether of o-cresol was prepared by the method described for the preparation of the allyl ether of phenol [4,9]. It boiled at 76-77° (4 mm).

n_D^{20} 1.5190; d_4^{20} 0.9658; MR_D 46.47; calculated 45.95. No active hydrogen was contained in the substance.

15.6 g of 65% peroxyacetic acid was added to 20 g of the allyl ether of o-cresol in 40 ml of anhydrous ether. No evolution of heat occurred; however the reaction mixture acquired a straw-yellow color. After 22 days no peroxide was present in the mixture. The reaction products were treated analogously to those in the preceding experiments.

Upon fractional distillation of the oxidation products at 8.5 mm, the bulk distilled over at 82-84°. This proved to be o-cresol. The arylglycolic acid obtained from it had a m.p. of 154°. A mixed sample with a preparation obtained by a known method gave no melting point depression. Only a total of 0.5 g of a substance with a b.p. of 129-131° (8.5 mm) was obtained; it was apparently the oxide of the allyl ether of o-cresol (II).

n_D^{20} 1.5270; d_4^{20} 1.0905; MR_D 46.24; calculated 45.29.

0.1900 g sub.: 0.5011 g CO_2; 0.1267 g H_2O. 0.1173 g sub.: 21.21 g benzene: Δt 0.182°. Found %: C 71.93; H 7.46; M 156.7. $C_{10}H_{12}O_2$. Calculated %: C 73.10; H 7.30; M 164.

The substance contained an insignificant admixture which contained active hydrogen; this was reflected in the analytical results.

Oxidation of o-Allyl-o-cresol with Peroxyacetic Acid

The o-allyl-o-cresol was prepared analogously to the o-allylphenol [4].

B.p. 92-94° (6 mm); n_D^{20} 1.5377; d_4^{20} 1.0010; MR_D 46.22; calculated 46.83.

15.6 g of 93% peroxyacetic acid was added to 28 g of the substance in 56 ml of dry ether. The oxidation proceeded smoothly, the temperature increased slowly and the color of the mixture became bright orange. After 3 days the oxidation was completed. The reaction products were treated analogously to those of the preceding experiments and vacuum distilled. 8 g of substance (V) with a bright orange color was obtained.

B.p. 146° (10 mm); n_D^{20} 1.5468; d_4^{20} 1.1213; MR_D 46.37; calculated 45.18.

0.2564 g sub.: 0.6910 g CO_2; 0.1710 g H_2O. 0.1208 g sub.: 15.92 ml CH_4 (0°, 760 mm). 0.1005, 0.2358 g sub.; 16.47 g benzene: Δt 0.175, 0.425°. Found %: C 73.50; H 7.46; OH 10.07; M 175.7, 177.4. $C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.32; OH 10.3; M 164.

Reaction of the Oxide of o-Allyl-o-cresol with Acetic Anhydride

10 g of acetic anhydride was added to 2 g of the substance and the mixture was boiled for 5 hours in a flask equipped with a reflux condenser. The acetic anhydride was distilled off in a vacuum and 1.2 g of substance (VIII) was obtained by fractional distillation of the reaction products.

B.p. 128-129° (2 mm); n_D^{20} 1.5045; d_4^{20} 1.1230; MR_D 54.35; calculated 54.54.

0.2050, 0.1483 g sub.: 0.5044, 0.3677 g CO_2; 0.1277, 0.0955 g H_2O. 0.1192, 0.2206 g sub.: 15.3 g benzene; Δt 0.223, 0.415°. Found %: C 67.10, 67.62; H 6.96, 7.20; M 179.2, 178.6. $C_{12}H_{14}O_3$. Calculated %: C 69.9; H 6.79; M 206. The test for active hydrogen was negative.

A repeated experiment involving the preparation of the acetyl derivative did not give better analytical results. Apparently, the reaction products are partially changed during the distillation.

Oxidation of o-Propenyl-o-cresol with Peroxyacetic Acid

o-Propenyl-o-cresol was prepared analogously to o-propenylphenol. It boiled at 125-127° (10 mm). It partially crystallized on standing. 35 g of o-propenyl-o-cresol was dissolved in 80 ml of anhydrous ether and oxidized with 24 g of 73% peroxyacetic acid. The reaction proceeded very energetically with marked evolution of heat. After 3 days there proved to be no peroxide in the mixture. The reaction products were treated as indicated for the preceding cases, and after drying with $MgSO_4$, were distilled. 10 g of an orange colored oily substance (VI) with the odor of phenol was obtained.

B.p. 141-143° (11 mm); n_D^{20} 1.5395; d_4^{20} 1.1030; MR_D 46.61; calculated 45.18.

0.1268 g sub.: 0.3415 g CO_2; 0.0851 g H_2O. 0.1679 g sub.: 25.46 ml CH_4 (0°, 760 mm). 0.1084, 0.2317 g sub.: 18.80 g benzene: Δt 0.185, 0.385°. Found %: C 73.45; H 7.53; OH 11.5; M 160.1, 164.5. $C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31; OH 10.36; M 164.

Preparation of 2,7-Dimethylbenzofuran

2 g of the oxide of o-propenyl-o-cresol was placed in a desiccator over sulfuric acid. The liquid became mobile and acquired a brown color overnight. 1.4 g of a mobile yellowish liquid (X) was obtained by its distillation.

B.p. 72° (3 mm); n_D^{20} 1.5540; d_4^{20} 1.0440; MR_D 44.82; calculated 43.75.

0.1266 g sub.: 0.3808 g CO_2; 0.0777 g H_2O. 0.1217, 0.2197 g sub.; 18.9 g benzene: Δt 0.225, 0.416°. Found %: C 82.08; H 6.87; M 147.1, 143.4. $C_{10}H_{10}O$. Calculated %: C 82.10; H 6.85; M 146. A test for hydroxyl groups was negative.

Reaction of the Oxide of o-Propenyl-o-cresol with Acetic Anhydride

3 g of the oxide and 10 g of acetic anhydride were boiled for 4 hours. 1.0 g of a readily mobile liquid (X) was obtained by distilling the reaction products.

B.p. 70-71° (3 mm); n_D^{20} 1.5515; d_4^{20} 1.0375; MR_D 44.65; calculated 43.75. Found %: C 82.20; H 7.30. $C_{10}H_{10}O$. Calculated %: C 82.10; H 6.85.

SUMMARY

1. The α-oxides of the allyl ether of phenol, o-allylphenol, o-allyl-o-cresol, o-propenylphenol and o-propenyl-o-cresol were prepared by the oxidation of the allyl and propenyl derivatives of phenol with peroxyacetic acid.

2. The allylphenol oxides were not altered by the action of zinc chloride, while upon heating with acetic anhydride they were acetylated at the phenolic hydroxyl group with formation of oxidoacetates.

3. The oxides of o-propenylphenols yield cumarone derivatives as a result of the action of dehydrating substances. The formation of compounds of the furan series from oxides of the o-propenylphenols proceeds via a preliminary conversion of the oxides into their unsaturated tautomeric phenol alcohols.

4. The conversion of oxides of o-propenylphenols into cumarone derivatives confirms the presence of oxido-enolic tautomerism in the alcohol oxides.

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* See Consultants Bureau Translation, p. 231

** See Consultants Bureau Translation, p. 503.

*** See Consultants Bureau Translation, p. 681.

OXIDATION OF TERTIARY α-KETO ALCOHOLS BY MANGANESE TRIACETATE

S. Zonis

As the author and a coworker have shown [1], during the oxidation of α-glycols with manganese triacetate, rupture of the carbon skeleton occurs regardless of the character of the alcoholic groups; a mechanism was proposed for the reaction. To confirm the hypothetical mechanism we investigated the oxidation of secondary α-keto alcohols. If the formation of glycolate occurs as an intermediate product in the oxidation process, then the secondary α-keto alcohols should be oxidized with retention of the carbon skeleton (with formation of an α-diketone), even in the presence of excess oxidant; the tertiary α-keto alcohols, on the other hand, must be oxidized only with rupture of the carbon skeleton (with formation of netural and acidic products).

Our investigations of the oxidation of tertiary α-keto alcohols of the aromatic phenylbenzoin and phenylanisoin series confirmed our hypotheses.

Diphenylketone and p-methoxydiphenylketone were isolated from the neutral reaction products as a result of the oxidation of these α-keto alcohols. Benzoic and anisic acid were isolated from the acidic products.

EXPERIMENTAL

Phenylbenzoin was prepared from benzil and phenylmagnesium bromide by the method described by S. Akri [2], with a m.p. of 86-87° (from ligroin).

Phenylanisoin was prepared from anisil and phenylmagnesium bromide. Inasmuch as phenylanisoin has not been described in the literature, we present the description of one of the experiments.

Phenylmagnesium bromide was prepared in the usual way from 1.3 g of magnesium and 9 g of bromobenzene. The phenylmagnesium bromide was added in the form of drops to a cooled ethereal solution of anisil (made from 7 g of anisil in 300 ml of anhydrous ether). Upon completion of the addition of the organomagnesium complex, the reaction mixture was stirred for 2 days at room temperature and then heated on a water bath for 1 hour. The warm ethereal solution was decanted from the unreacted anisil. The ethereal solution was dried with roasted sodium sulfate. After distilling off a portion of the ether, a yellow crystalline precipitate consisting of unreacted anisil settled out. Two substances were isolated from the filtrate by fractional crystallization – one with a m.p. of 86-95°, the other with a m.p. of 93-95°. After two-fold crystallization of the latter from methyl alcohol, crystals with a m.p. of 94-95.5°, were isolated. A mixed sample with anisil melted (not sharply) at 85-115°.

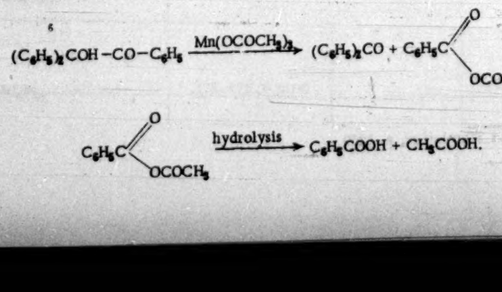
Analysis of the crystalline substance with a m.p. of 94-95°:

0.1258 g sub.: 0.3503 g CO_2; 0.0615 g H_2O. 0.3039 g sub.; 22.23 g benzene: Δt 0.204°: 0.1063 g sub.: 6.74 ml CH_4(22°, 764.2 mm). Found %: C 75.95; H 5.47; M 335.8. $C_{22}H_{20}O_4$. Calculated %: C 75.86; H 5.74; M 348.0; 6.83 ml CH_4.

It can be concluded on the basis of the analytical data that the crystalline substance with a m.p. of 94-95.5° is phenylanisoin.

Oxidation of Phenylbenzoin

The equation of the oxidation reaction can be depicted by the following scheme:



$$(C_6H_5)_2COH-CO-C_6H_5 \xrightarrow{Mn(OCOCH_3)_3} (C_6H_5)_2CO + C_6H_5C(=O)OCOCH_3$$

$$C_6H_5C(=O)OCOCH_3 \xrightarrow{\text{hydrolysis}} C_6H_5COOH + CH_3COOH.$$

We present the description of one of the experiments involving the oxidation of 1 g of phenylbenzoin with a m.p. of 86-87°, 2.4 g of manganese triacetate (68%) in 100 ml of glacial acetic acid.

The reaction mixture was heated on a boiling water bath for 10 hours and then a portion of the acetic acid (75 ml) was distilled off and the residue poured into water. The aqueous solution was neutralized with potash and steam distilled to isolate the neutral products. An ethereal extract was made from the aqueous distillate and after drying over sodium sulfate the ether was distilled off; 0.6 g of a viscous oily liquid was left in the flask. Upon seeding with a crystal of diphenylketone, the entire liquid crystallized, m.p. 47-48°. A mixed sample with known diphenylketone did not give any lowering of the melting temperature.

The aqueous solution left after distilling off the diphenylketone was acidified with nitric acid, and secondarily steam distilled to eliminate the acetic acid. A test with hydrogen peroxide and ferric chloride qualitatively disclosed the presence of benzoic acid in the distilled liquid.

After the steam distillation of the acetic acid, the aqueous solution left in the distilling flask was treated with ether to extract the benzoic acid. The etheral extract was saturated with ammonia after drying over fused sodium sulfate and then treated with a concentrated solution of silver nitrate; the silver salt thereupon precipitated.

0.1697 g salt: 0.0803 g Ag. Found %: Ag 47.31. $C_7H_5O_2Ag$. Calculated %: Ag 47.13.

Oxidation of Phenylanisoin

The oxidation proceeds according to a scheme analogous to that for the oxidation of phenylbenzoin.

1.04 g of phenylanisoin with a m.p. of 94-95.5°, 2.1 g of manganese triacetate (68%) and 100 ml of glacial acetic acid were taken. The reaction conditions for the oxidation were the same as those for the oxidation of phenylbenzoin. After steam distillation, 0.52 g of a substance was isolated which crystallized from alcohol in the form of shiny needles, with a m.p. of 59.5-60.5°.

To characterize the p-methoxydiphenylketone, the oxime with a m.p. of 116-117° was prepared (from alcohol) by the usual method; its m.p. was in accord with the literature data [3].

The aqueous solution left after steam distilling the p-methoxydiphenylketone, was acidified with nitric acid and secondarily steam distilled to eliminate the acetic acid. Anisic acid which melted at 182-183° (from water) was left in the distilling flask after eliminating the acetic acid. According to the literature data, the melting point of anisic acid is 184.4° [4].

The anisic acid was converted into the silver salt to characterize it:

0.1679 g salt: 0.0702 g Ag. Found %: Ag 41.81. $C_8H_7O_3Ag$. Calculated %: Ag 41.68.

SUMMARY

Tertiary α-keto alcohols are oxidized only with rupture of the carbon skeleton, which is in accord with the reaction mechanism previously proposed.

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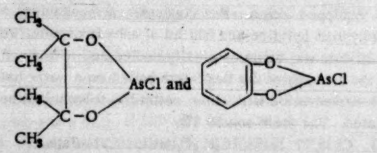
THE ACID CHLORIDES AND MIXED ESTERS OF TETRAMETHYLENEGLYCOLARSENOUS AND PYROCATECHOLARSENOUS ACIDS

Gilm Kamai and Z. L. Khisamova

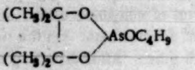
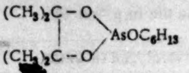
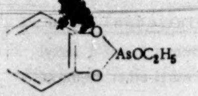
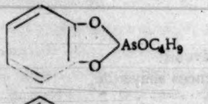
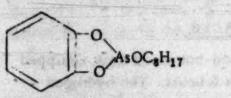
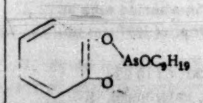
Work on the synthesis of various cyclic acid chlorides and mixed esters of α-glycolarsenous and β-glycolarsenous acids [1,2] was begun in our laboratory in 1951.

In a continuation of this investigation, we synthesized the following cyclic acid chlorides for the first time:

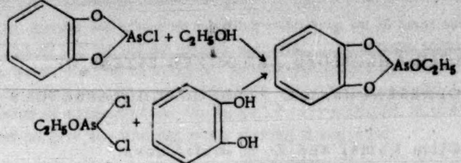


The acid chlorides isolated were crystalline substances, soluble in water and certain organic solvents. When kept for a long time, hydrolysis of the aqueous solutions of the acid chlorides occurs with formation of arsenous anhydride and the corresponding dihydroxy compounds.

We obtained mixed esters by the reaction of the indicated acid chlorides with various alcohols in the presence of substances which bind HCl. Certain data concerning them is set forth in the table.

No.	Formula	Boiling point	Melting point	d_0^{20}	n_D^{20}
1		–	94°	–	–
2		133° (8 mm)	–	1.2306	1.4622
3		116–117 (10 mm)	148–150	–	–
4		140 – 141 (14 mm)	–	1.3634	1.5400
5		164–165 (4.5 mm)	–	1.2241	1.5182
6		175–176 (5 mm)	–	1.2005	1.5150

For comparison, we synthesized the ethyl ester of pyrocatecholarsenous acid by the two following methods:



EXPERIMENTAL

Preparation of the Acid Chloride of Tetramethylethyleneglycolarsenous Acid

In a round-bottomed flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel, 44.3 g. of pinacol, 59.3 g. of anhydrous pyridine and 500 ml of anhydrous ether were placed. 67.6 g. of arsenic trichloride was added while the mixture was being externally cooled and stirred. After the addition of the entire quantity of arsenic trichloride, the contents of the flask were boiled on a water bath for 30 minutes. The precipitate was then filtered off and washed twice with ether. After the solvent had been distilled off, white crystals with a m.p. of 121° precipitated. The yield was 53.4%.

Found %: As 33.29, 33.23; Cl 15.77 15.63. $C_6H_{12}O_2AsCl$. Calculated %: As 33.06; Cl 15.61.

The acid chloride of tetramethylethyleneglycolarsenous acid was quite soluble in water, acetone, benzene, chloroform, dioxane, and more difficultly soluble in gasoline and xylene.

Saponification of the Acid Chloride of Tetramethylethyleneglycolarsenous Acid

1 g of the acid chloride was stirred with 30 ml of water and left overnight. On the next day the white precipitate which was formed was filtered off, washed with water, dried to constant weight and analyzed.

Found %: As 75.52. As_2O_3. Calculated %: As 75.74.

Preparation of the n-Butyl Ester of Tetramethylethyleneglycolarsenous Acid

10 g of the acid chloride of tetramethylethyleneglycolarsenous acid was added through a dropping funnel to a solution of 3.62 g of n-butyl alcohol, 3.5 g of anhydrous pyridine and 300 ml of anhydrous ether. After the introduction of all the acid chloride, the contents of the flask were heated on a water bath. On the next day the precipitate – pyridine hydrochloride – was filtered off and washed with ether. After distilling off the solvent, the liquid which was left was vacuum distilled. A fraction with a b.p. of 170-190° at 12 mm, which crystallized on standing, was isolated. After recrystallization from toluene the m.p. was 94°.

Found%: As 28.46, 28.43. $C_{10}H_{21}O_3As$. Calculated %: As 28.36.

The ester isolated was soluble in many of the usual organic solvents. It hydrolyzed in water.

Preparation of the n-hexyl Ester of Tetramethylethyleneglycolarsenous Acid

The n-hexyl ester of tetramethylethyleneglycolarsenous acid was synthesized from 2.5 g of n-hexyl alcohol and 5 g of the acid chloride of tetramethylethyleneglycolarsenous acid in an ethyl ether medium in the presence of 1.75 g of pyridine.

B.p. 133° at 8 mm; d_0^0 1.2515; d_0^{20} 1.2306; n_D^{20} 1.4622.

Found: As 25.83, 25.72. $C_{12}H_{25}AsO_3$. Calculated %: As 25.63

The ester obtained consisted of a colorless liquid, soluble in many organic solvents.

It was comparatively readily saponified with water with the formation of arsenous anhydride.

Preparation of the Acid Chloride of Pyrocatacholarsenous Acid

15 g of pyrocatechol and 25.6 g of arsenic trichloride were placed in a round-bottomed flask equipped with a reflux condenser. The contents of the flask were heated on an oil bath for 5 hours. The hydrogen chloride which was evolved was trapped with water. The remaining mass was heated in a sealed tube at 200° for 3 hours. After cooling the tube was opened. A crystalline substance with a m.p. of 133° was obtained after recrystallization from toluene. The yield was 24.2 g (61%).

Found %: As 34.46, 34.53; Cl 16.48, 16.36. $C_6H_4O_2AsCl$. Calculated %: As 34.30; Cl 16.23.

The acid chloride obtained was quite soluble in water, ether, acetone, benzene, chloroform, dioxan, and more difficultly soluble in toluene, xylene, and gasoline. It was saponified very slowly by water.

Saponification of the Acid Chloride of Pyrocatecholarsenous Acid

A mixture of 1 g of the acid chloride and 30 ml of water was heated in a flask equipped with a reflux condenser for 6 hours. On the next day the white precipitate which was formed was filtered off, washed and dried to constant weight.

Found %: As 75.55. As_2O_3. Calculated %: As 75.74

The presence of pyrocatechol was qualitatively detected in an aqueous solution.

Preparation of the Ethyl Ester of Pyrocatecholarsenous Acid

Experiment 1. 20 g of the acid chloride of pyrocatecholarsenous acid was added through a dropping funnel to a solution, cooled to 0° and stirred, of 5 g of anhydrous ethyl alcohol, 7.3 g of anhydrous pyridine and 350 ml of benzene. The contents of the flask were boiled on a water bath for 30 minutes. After cooling, the precipitate was filtered off and washed with benzene. The mass left after distilling off the benzene was then subjected to vacuum distillation. 9.6 g (46%) of a fraction with a b.p. of 114° at 10 mm was isolated. It crystallized on standing. The melting point of the crystals was 150°.

Found %: As 32.95. $C_8H_9O_3As$. Calculated %: As 32.85. Found: M 230.2 (by Rast's method). $C_8H_9O_3As$. Calculated: 228.1.

Experiment 2. The ethyl ester of pyrocatecholarsenous acid was prepared by the mutual reaction of 7.4 g of pyrocatechol, 10.6 g of anhydrous pyridine and 12.8 g of ethoxydichloroarsine in an anhydrous ethyl ether medium. After the usual treatment of the reaction products and vacuum distillation, a basic fraction with a b. p. of 116-117° at 10-11 mm and a m.p. of 148-149° was isolated.

Found %: As 32.88, 32.79. $C_8H_9O_3As$. Calculated %: As 32.85.

The ethyl ester of pyrocatecholarsenous acid was soluble in many organic solvents.

Saponification of the Ethyl Ester of Pyrocatecholarsenous Acid

8 g of the ethyl ester of pyrocatecholarsenous acid was stirred with 50 ml of water. The saponification reaction proceeded energetically with the formation of a white precipitate. The presence of pyrocatechol was qualitatively detected in the aqueous solution. The precipitate was filtered off, washed several times with water and once with alcohol. After it had been dried to constant weight, it was analyzed.

Found %: As 75.49 As_2O_3. Calculated %: As 75.73.

Preparation of the n-Butyl Ester of Pyrocatecholarsenous Acid

The compound was prepared by the mutual reaction of 4 g of n-butyl alcohol, 3.7 g of pyridine and 10 g of the acid chloride in a benzene medium. After treatment of the reaction products and vacuum distillation, 4.2 g (35.8%) of a colorless liquid was isolated. Water hydrolyzed it.

B. p. 140-141° at 14 mm; d_0^0 1.3837; d_0^{20} 1.3634; n_D^{20} 1.5400

Found %: As 28.94, 29.08. $C_{10}H_{13}O_3As$. Calculated %: As 29.25

Preparation of the n-Octylpyrocatechol Ester of Arsenous Acid

3.8 g of the n-octylpyrocatechol ester of arsenous acid was obtained in the form of a colorless liquid from 4 g of n-octyl alcohol, 2.5 g. of anhydrous pyridine and 6 g of the acid chloride in a benzene medium.

B. p. 164-165° at 4.5 mm; d_0^0 1.2426; d_4^{20} 1.2241; n_D^{20} 1.5182.

Found %: As 23.79, 23.81. $C_{14}H_{21}O_3As$. Calculated %: As 23.99.

Preparation of the n-Nonylpyrocatechol Ester of Arsenous Acid

4.5 g of n-nonyl alcohol, 2.5 g of anhydrous pyridine, 6.1 g of the acid chloride of pyrocatecholarsenous acid and 200 ml of benzene were taken for the reaction. After vacuum distillation, 4.2 g of a thick colorless liquid, quite soluble in organic solvents, was obtained.

B. p. 175-176° at 5 mm; d_0^0 1.2184; d_0^{20} 1.2005 ; n_D^{20} 1.5150. MR_D 81.94. $C_{15}H_{23}O_3As$. Calc. 81.53.

Found %: As 22.79, 22.85. $C_{15}H_{23}O_3As$. Calculated %: As 22.96.

SUMMARY

1. The acid chlorides of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids were prepared and studied for the first time.

2. By the reaction of these acid chlorides with various alcohols in a benzene medium and in the presence of anhydrous pyridine, the mixed esters of tetramethyleneglycolarsenous and pyrocatecholarsenous acids were synthesized and their properties described.

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[1] Gilm Kamai and Z. L. Khisamova, Proc. Acad. Sci. USSR, 535 (1951).

[2] Gilm Kamai and Z. L. Khisamova. Proc. Acad. Sci. USSR, 81, 857 (1951); 86, 71 (1952); Bull. Acad. Sci. USSR, Div. Chem. Sci., 908 (1952).

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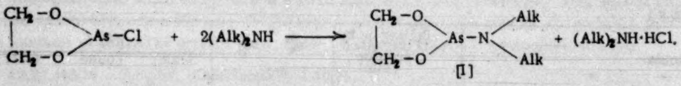
THE REACTION OF CYCLIC ACID CHLORIDES OF ARSENOUS ACID WITH DIALKYLAMINES

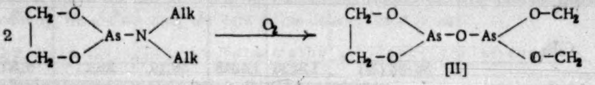
Gilm Kamai and Z. L. Khisamova

Substituted amido esters of arsenous acid with the >As – N< bond have hitherto not been described. In the present communication, data are presented on the synthesis of the first few representatives of this group, of specifically cyclic dimethyl- and diethyl-substituted amido esters of arsenous acid.

We took the previously synthesized cyclic acid chlorides of ethyleneglycolarsenous, tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids [1] as subjects for the investigation and let them react in an inert solvent with timethylamine or diethylamine. In the reaction of the acid chloride of ethyleneglycolarsenous acid with dialkylamines in a medium of dry benzene, the reaction fundamentally goes in the direction of forming dialkyl-substituted amides of the cyclic esters of arsenous acid (I) according to the scheme:



It will also become clear that during this reaction, in addition to the dialkyl substituted amidoesters of arsenous acid, a considerable quantity of the ethyleneglycolic ester of pyroarsenous acid (II) was formed. The formation of the latter as an oxidation product with rupture of the >As – N< bond can be represented by the following scheme:



We did not study the nitrogen-containing portion of this reaction in detail.

It is of interest to note that, in the reaction of the acid chlorides of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids with dialkylamines under analogous reaction conditions and in an atmosphere of air, we isolated only the corresponding esters of pyroarsenous acid.

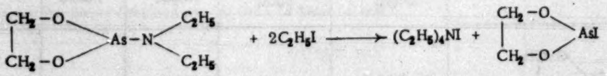
We accomplished the synthesis of dialkyl substituted amido esters of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids by the action of the corresponding acid chlorides on dialkylamines in a medium of inert solvent and in a stream of nitrogen.

The dialkyl-substituted amido esters of arsenous acid synthesized by us are presented in Table 1.

The amido esters isolated were colorless liquids. They were oxidized in air with rupture of the >As – N< bond and formation of the corresponding esters of pyroarsenous acid (Table 2).

The pyroarsenous esters investigated were comparatively readily saponified by water.

We then studied the reaction between ethyl iodide and the diethylamido ester of ethyleneglycolarsenous acid. The experiments showed that the indicated substances react in the cold and in an ether medium according to the following scheme:



EXPERIMENTAL

Preparation of the Dimethylamide of Ethyleneglycolarsenous Acid

26.4 g of freshly distilled diethylamine and 100 ml of dry benzene were placed in a flask with a reflux condenser, mechanical stirrer and dropping funnel. The flask was externally cooled with snow. A solution of 50 g of the acid chloride of ethyleneglycolarsenous acid in 100 ml of benzene was added from the dropping funnel. Upon completion of the reaction, dimethylamine hydrochloride was separated by centrifuging.

The mass which was left after distilling off the benzene from the filtrate was subjected to vacuum distillation. Two fractions were isolated after 2-fold distillation.

The first fraction, 13.9 g (26.7%) consisted of a colorless, readily mobile liquid with a weak amine odor.

B. p. 101-102° at 55 mm; d_4^{20} 1.4643; n_D^{20} 1.5030; MR_D 36.14; Calc. 36.32.
Found %: As 41.57; N 7.35; $C_4H_{10}O_2AsN$. Calculated %: As 41.82; N 7.81.

The dimethylamide of ethyleneglycolarsenous acid was soluble in many organic solvents. It was hydrolyzed by water with the formation of arsenous anhydride.

The second fraction was a colorless, thick liquid with no odor:
B.p. 172-175° at 18 mm; d_4^{20} 2.0221; n_D^{20} 1.5569; MR_D 45.72; Calc. 45.42.
Found %: As 51.95, 51.89. $C_4H_8O_5As_2$. Calculated %: As 52.40.

The analytical data indicate that the second fraction was the comparatively pure ethyleneglycol ester of pyroarsenous acid (II). The ester was saponified by water with the formation of ethyleneglycol and arsenous anhydride.

TABLE 1

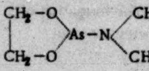
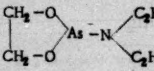
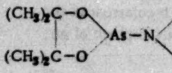
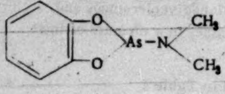
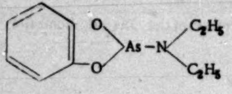
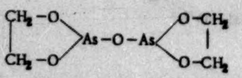
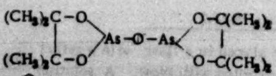
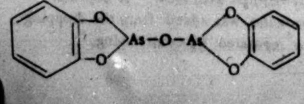
Formula	Boiling point at the given pressure (mm)	d_4^{20}	n_D^{20}	As (%)		N (%)		Yield (%)
				Calc.	Found	Calc.	Found	
	101-102° (55)	1.4643	1.5030	41.84	41.64	7.83	7.13	26.7
	85-86 (12)	1.3535	1.4948	36.10	36.11	6.57	6.79	58.0
	94 (16)	1.2345	1.4810	31.80	32.07	5.96	5.78	70.0
	146 (26)	1.4795	1.5868	33.00	32.76	–	–	26.3
	149 (17)	1.3620	1.5608	29.34	29.48	5.47	5.05	28.3

TABLE 2

Formula	Boiling point at pressure (mm)	Melting point	As (%)		Notes
			Calc.	Found	
	122-123° (1)	–	52.40	51.89	Liquid
	142 (3)	97°	37.42	37.39	Colorless Crystals
	–	147	39.0	38.79	Colorless Crystals

The preparation of the diethylamide of ethyleneglycolarsenous acid was carried out by the method described above, starting with 20 g of the acid chloride of ethyleneglycolarsenous acid, 17.2 g of diethylamine and 250 ml of ethyl ether. The following were obtained as a result of two-fold fractional distillation:

14.2 g of the first fraction. This consisted of a readily mobile colorless liquid which was soluble in many organic solvents. It was hydrolyzed by water:
B. p. 88-89° at 17 mm; d_4^{20} 1.3442; n_D^{20} 1.4918.
Found %: As 35.83; N 6.75. $C_6H_{14}O_2AsN$. Calculated %: As 36.10; N 6.98.

The second fraction:
B. p. 172-173° at 18 mm; d_4^{20} 2.0245; n_D^{20} 1.5569.
Found %: As 52.09. $C_4H_8O_5As_2$. Calculated %: As 52.40.

Thus, the ethyleneglycol ester of pyroarsenous acid was also isolated during this reaction.

Reaction of the diethylamide of ethyleneglycolarsenous acid with ethyl iodide.

4.3 g of ethyl iodide was added to a cooled mixture of 5.8 g of the diethyamide of ethyleneglycolarsenous acid and 50 ml of anhydrous ether which was placed in a small flask with a reflux condenser. After several minutes a crystalline precipitate began to settle out. On the next day the crystals were filtered off, washed with ether and dried to constant weight. The crystals were soluble in water and alcohol and insoluble in ether.

Found %: I 49.27, 49.19. $C_8H_{20}NI$. Calculated %: I 49.00.

Nitrogen was qualitatively detected; arsenic was absent. The compound obtained consisted of tetraethylammonium iodide according to the analytical data.

A fraction with a b.p. of 150-152° at 10 mm was separated by vacuum distilling from the liquid portion of the reaction products. We did not study the light yellow colored liquid in detail.

Reaction of the Acid Chlorides of Tetramethylethyleneglycolarsenous and Pyrocatecholarsenous acids with Dialkylamines

Experiment 1. 15.12 g of the acid chloride of tetramethylethyleneglycolarsenous acid, dissolved in benzene, was added to a stirred solution of 6 g of dimethylamine in 30 ml of dry benzene. The precipitate of dimethylamine hydrochloride which settled out was filtered off. After distilling off the solvent from the filtrate the mass which was left was subjected to vacuum fractional distillation. A fraction with a b.p. of 142° at 3 mm which rapidly crystallized was isolated. The crystals were soluble in many organic solvents. M.p. 97°.

Found %: As 37.39, 37.45. $C_{12}H_{24}O_5As_2$. Calculated %: As 37.63.

We did not succeed in isolating other individual substances.

Experiment 2. By the reaction of the corresponding quantities of the acid chloride and dimethylamine according to the method indicated above, but in a jet of nitrogen, a fraction was isolated in the form of a colorless liquid:

B. p. 94° at 16 mm: d_4^{20} 1.2345; n_D^{20} 1.4810 ; MR_D 54.22; Calc. 54.71
Found %: As 32.07; N 5.78. $C_8H_{18}O_2AsN$. Calculated %: As 31.86; N 5.96.

The preparation of the two dialkylamidopyrocatecholarsenous esters and the pyrocatechol ester of pyroarsenous acid was carried out according to the method described above.

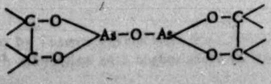
The data on the esters obtained are set forth in Tables 1 and 2.

SUMMARY

1. Dialkyl substituted amides of the cyclic esters of arsenous acid were synthesized for the first time.

2. It was shown that the $>As-N<$ bond is very unstable in these compounds and is disrupted by the action of alkyl halide, atmospheric oxygen and water.

3. It was established that the product of the oxidation of the dialkylamido esters of arsenous acid consists of cyclic esters of pyroarsenous acid with the following composition:



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[1] Gilm Kamai and Z. L. Khisamova, Proc. Acad. Sci. USSR, 46, 535 (1951); Gilm Kamai and N. A. Chadaeva, Proc. Acad. Sci. USSR, 81, 857 (1951); 86, 41 (1952).

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ALKYLATION OF BENZENE BY ALIPHATIC ALCOHOLS AND HALOGEN DERIVATIVES OVER ALUMINO-SILICATE CATALYSTS

B. N. Dolgov and A. S. Cherkasov

The number of published works devoted to the vapor phase catalytic alkylation of aromatic hydrocarbons by alcohols and alkyl halides is remarkably small. What has been investigated is chiefly alkylation with methyl and ethyl alcohols * and with methyl chloride. The yields of alkyl substituted aromatic hydrocarbons obtained by alkylation with these reagents at atmospheric pressure, does not exceed 10-15% of the theoretical yield [1,2,3]. Only by conducting the reaction under pressure was a yield up to 30% of the theoretical successfully obtained [4]. Vapor phase alkylation with alcohols and halogen derivatives is accomplished with the aid of catalysts, of which the most effective are the aluminosilicate [1,2,3,5,6,7] and phosphoric acid or its salts [4,8,9].

From 1947 on, work on the study of the alkylation of aromatic hydrocarbons with alcohols and halogen derivatives over aluminosilicate catalysts has been carried out in the Department of Organic Chemistry at Leningrad University. The results obtained constitute the material for a bachelor's thesis presented by one of us in 1950. We investigated the alkylation of benzene with ethyl, n-propyl, isopropyl and isopropyl bromides, and isobutyl bromide. The alkylation was carried out over an aluminosilicate catalyst at atmospheric pressure in the usual apparatus used in the investigation of vapor phase catalytic reactions under dynamic conditions.

Alkylation with Alcohols

The reaction between benzene and isopropyl alcohol proceeds most readily. The reaction products are isopropylbenzene and polyalkylbenzenes (chiefly p-diisopropylbenzene), and also propylene and water which are formed as a result of the dehydration of isopropyl alcohol. Small quantities of saturated hydrocarbons (1-3%) and hydrogen (0.5-1.5%) are also contained in the gaseous reaction products, in addition to propylene. The formation of polyalkylbenzenes is markedly diminished by conducting the reaction with a great excess of benzene. Thus, the content of polyalkylbenzenes in the alkylbenzene fraction is equal to 20-30% at a molar ratio of benzene to alcohol of 2:1, while on increasing this ratio to 4:1, their content falls to 5-10%.

The optimal temperature for alkylating benzene with isopropyl alcohol is a temperature of 300-320° (Fig 1, curves I and II) at which the yield of isopropylbenzene reaches 52% of the theoretical (calculating on the basis of the alcohol passed) at a rate of supplying the reaction mixture (v) of 0.5 ml per 1 ml of catalyst per hour (curve I) and 60% at a rate of supply of 0.25 ml (curve II). Reducing the experimental temperature to 260° almost halves the rate of alkylation. Increasing the temperature above 320° also leads to a reduction in the yield of isopropylbenzene. Since no other new reaction products were formed in this case, while only the quantity of propylene formed was increased, it must be considered that at temperatures above 320° thermodynamic equilibrium is reached in our experiments between the starting materials and the reaction products. This is also confirmed by the fact that at temperatures of 340° and higher the yield of isopropylbenzene, obtained at a supply rate of 0.5 ml/ml per hour, is practically equal to the yield obtained at a rate of 0.25 ml/ml per hour.

The rate of the alkylation of benzene with n-propyl alcohol is somewhat less than the rate of alkylation with isopropyl alcohol: the yields of propylbenzene obtained at temperatures lower than the optimal (i.e., at temperatures at which the yield of propylbenzene is determined by the reaction rate and not by thermodynamic equilibrium) is always less in alkylation with n-propyl alcohol (Fig. 1, curve III). During alkylation with n-propyl alcohol, isomerization of the propyl group occurs in the course of the reaction, and it is not n-propylbenzene, but isopropylbenzene which appears as the reaction product, as in alkylation with isopropyl alcohol. On the basis of the fact that over aluminosilicate catalysts alcohols are readily dehydrated, being converted into olefins (isopropyl alcohol, for example, is practically completely dehydrated to propylene even at 240-250° [12] while olefins alkylate aromatic hydrocarbons over the same catalysts,

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* Works by Turova-Polyak with her coworker [10] and Shuikin and his coworkers [11] have recently been published in which alkylation with higher alcohols has been investigated.

it seems very probable to us that alkylation with alcohols proceeds via intermediate formation of olefins. On the other hand, the fact that aromatic hydrocarbons can be alkylated with methyl alcohol indicates that a route of direct alkylation by alcohol which skips the stage of olefin formation, is not excluded. Actually, it is evident that both reactions can proceed parallelly in the alkylation with alcohols. If alkylation of benzene with alcohol proceeds only via intermediate olefin formation, then it must be expected that higher yields of alkylbenzene will be obtained in alkylation with olefins than in alkylation under the same conditions with the corresponding alcohols. The results of the experiments carried out by us involving the alkylation of benzene with propylene at various temperatures are presented in Fig. 1 (curve IV). As is evident from the data of the figure, at a temperature below 300° the yields of isopropylbenzene obtained in alkylation with propylene are actually higher than in alkylation with n-propyl alcohol. However, in alkylation with n-propyl alcohol at a temperature above 300°, and also in alkylation with isopropyl alcohol at various temperatures, higher yields are obtained than in alkylation with propylene. The difference in the yields of isopropylbenzene is particularly noticeable at low rates of supply of the reaction mixture (Fig. 2). Thus, at a rate of supply v = 0.25 ml/ml/hr and a temperature of 320° in alkylation with n-propyl and isopropyl alcohols, the yield of isopropyl benzene is equal to 58-60% (calculating on the basis of alcohol passed) as against 43% in alkylation with propylene. The small increase in the yield of isopropylbenzene (from 33 to 43%) at a a 75% reduction in the rate of supply (from 1 to 0.25 ml/ml/hr) is characteristic of alkylation with propylene (Fig. 2, curve III), although the degree of conversion calculated for this temperature according to the reaction $C_3H_6 + C_6H_6 \rightleftharpoons C_6H_5C_3H_7$ is equal to about 80%. In our opinion, this fact is to be explained by rapid deactivation of the catalyst during the alkylation with propylene. The data presented in Table 1 are evidence of the presence of catalyst poisoning during alkylation with propylene. As is evident from the data of Table 1, after passing 17 g of a mixture of benzene with propylene over the catalyst, the yield of isopropylbenzene is lowered by 7-8% at a supply rate of benzene of 0.4 ml/ml/hr (experiments 57a, b, c) and by 11% at a rate of supply of benzene of 0.2 ml/ml/hr. After regeneration of the catalyst its activity is completely regenerated. The process of catalyst poisoning during alkylation with isopropyl alcohol proceeds considerably more slowly (Table 2, experiments 59a, b, 60a, b).

TABLE 1

Expt. No.	Rate of supply of benzene (ml/ml/hr)	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
57a	0.4	17	42.5
57b	0.4	18	35.1
57c	0.4	17	26.9
58a	0.2	17	48.3
58b	0.2	17	37.1

Note: The temperature was 320°, the molar ratio $C_6H_6:C_3H_6$ = 4:1, the catalyst was 30 ml (9.5 g)

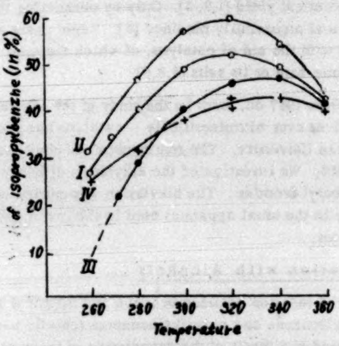

Fig. 1. I) Benzene + isopropyl alcohol, v = 0.5 0.5 ml/ml/hr; II) benzene + isopropyl alcohol, v = 0.25 ml/ml/hr; III) benzene + n-propyl alcohol, v = 0.5 ml/ml/hour; IV) benzene + propylene, v = 0.5 ml/ml/hr.

The yields of isopropylbenzene in alkylation with propylene over catalyst over which the alkylation with isopropyl alcohol has already been carried out, do not practically differ from the yields obtained for fresh or regenerated catalyst (experiments 59c and 60c). After carrying out alkylation with propylene, the catalyst also proved to be poisoned for the reaction of benzene with alcohol (experiments 59d and 60d).

We set up experiments in which the alcohol was decomposed over aluminosilicate catalyst by being passed through one oven and in which the propylene obtained, together with steam entered another oven to which benzene was also supplied. The yield of isopropylbenzene obtained by carrying out the experiments in this way, was no higher, and even somewhat lower (34%) than in the ordinary alkylation of benzene with propylene, i.e., the smaller poisoning and greater yield of isopropylbenzene in alkylation with alcohol in comparison with the yield obtained in alkylation with propylene, can evidently not be explained by the favorable action of steam. The direct cause of the deactivation of the catalyst is apparently the deposition on its surface of "coke" – highly unsaturated compounds which render the surface of the catalyst unsuitable for the reacting molecules. The formation of "coke", as has been shown

shown [13,14], is directly associated with the redistribution of hydrogen which proceeds readily during the contact of unsaturated hydrocarbons with aluminosilicate catalysts. Inasmuch as the rate of this reaction depends on the concentration of the unsaturated compounds (in our experiments on the concentration of propylene), which will be less in alkylation with alcohol than in alkylation with propylene, it can be assumed that the rate of deposition on the catalyst of substances which lead to its deactivation will also be less in alkylation with alcohol. It seems to us that this circumstance is one of the causes which facilitate the preparation of higher yields of isopropylbenzene in the alkylation of benzene with alcohol, as compared with alkylation with propylene. In addition, in the first case, as has already been indicated, the formation of alkylbenzenes, evidently can proceed not only due to the reaction of benzene with the propylene which is formed by the dehydration of the alcohol, but also due to its direct condensation with alcohol. If these two reactions proceed parallelly, this will also facilitate higher yields of alkylbenzenes.

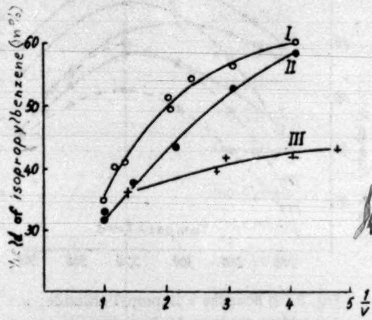

Fig. 2. I) Benzene and isopropyl alcohol; II) benzene + n-propyl alcohol; III) benzene + propylene. The temperature of the experiments was 320°; the molar ratio benzene : alcohol (propylene) = 4:1.

R

The alkylation of benzene with ethyl and butyl alcohols under conditions analogous to the conditions of the experiments involving the alkylation with propyl alcohols, hardly proceeds at all. In experiments with ethyl alcohol the yield of ethylbenzene amounted to about 4% of the theoretical; in alkylation with tertiary butyl alcohol only an insignificant quantity of tertiary butylbenzene was isolated; and in experiments with isobutyl alcohol no alkylbenzenes at all were obtained.

TABLE 2

Expt. No.	Alkylating agent	Rate of supply of the reaction mixture (benzene)	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
59a	iso-C_3H_7OH	0.5	16	48.2
59b	iso-C_3H_7OH	0.5	16	45.3
59c	$CH_3CH=CH_2$	0.4	17	38.9
59d	iso-C_3H_7OH	0.5	16	23.5
60a	iso-C_3H_7OH	0.2	18	63.1
60b	iso-C_3H_7OH	0.2	18	60.0
60c	$CH_3CH=CH_2$	0.2	17	44.5
60d	iso-C_3H_7OH	0.2	15	37.5
60e	$CH_3CH=CH_2$	0.15	17	26.0

Note: The temperature was 320°, the molar ratio C_6H_6: iso-C_3H_7OH = 4:1.

Alkylation with Alkyl Halides

It was found in the study of the alkylation of benzene with alkyl halides that high yields of alkylbenzenes were obtained only in the alkylations with isopropyl chloride, n-propyl bromide and isopropyl bromide. In the alkylation with ethyl bromide the yield of ethylbenzene amounted to not more than 10-15% of the theoretical, while in alkylation with isobutyl bromide only an insignificant quantity of tertiary butylbenzene was obtained.

Alkylation with isopropyl chloride, n-propyl bromide and isopropyl bromide was carried out at experimental temperatures of 260 to 360°, a rate of supply of the reaction mixture of 0.5 ml/ml of catalyst per hour, and a molar ratio of benzene to alkyl halide of 4:1. Under these conditions the chief alkylation product was propylbenzene; the quantity of polyalkylbenzenes (chiefly p-diisopropylbenzene) amounted to 10-15% of the total weight of the alkylbenzene fraction. Alkylation with normal propyl bromide was accompanied by isomerization of the alkyl group and the reaction product was isopropylbenzene, just as in alkylation with isopropyl chloride and isopropyl bromide.

The experimental data, found by us for the dependence of the yield of isopropylbenzene (in percentages of the theoretical yield) on the experimental temperature in alkylation with various propyl halides, are graphically presented in Fig. 3. The curves obtained in the alkylation with isopropyl alcohol are also set forth for comparison.

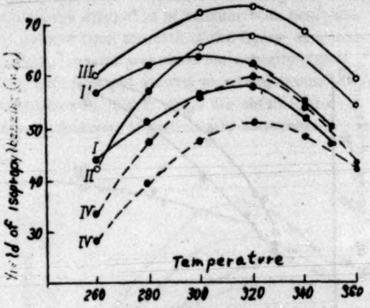

Fig. 3. I) Benzene + isopropyl chloride, v = 0.5 ml/ml per hour; I') benzene + isopropyl chloride, v = 0.25 ml/ml per hour, II) benzene + n-propyl bromide, v = 0.5 ml/ml per hour, III) benzene + isopropyl bromide, v = 0.5 ml/ml per hour; IV) benzene + isopropyl alcohol, v = 0.5 ml/ml per hour, IV') benzene + isopropyl alcohol, v = 0.24 ml/ml per hour.

As is evident from the data of Fig. 3, the alkylation of benzene with alkyl halides proceeds considerably more readily than alkylation with the corresponding alcohols: at 320° and a rate of 0.5 ml the yield of isopropylbenzene is equal to 59% in alkylation with isopropyl chloride, 67.5% with n-propyl bromide and 70-74% with isopropyl bromide as against 49-53% in alkylation with isopropyl alcohol. This difference in the rates of the alkylation reaction is particularly noticeable at an experimental temperature of 260°, at which the system is far removed from the equilibrium state. In this case, in alkylation with isopropyl alcohol the over-all yield of isopropylbenzene is equal to 27% of the theoretical, while in alkylation with isopropyl chloride it reaches 45% and with isopropyl bromide 60%.

At a temperature above 320° the curves which represent the results of the alkylation with isopropyl chloride, and with isopropyl alcohol, practically coincide. This is evidently to be explained by the fact that under these conditions the yield of isopropylbenzene is still determined by the thermodynamic equilibrium between isopropylbenzene, benzene and propylene. Carrying out the alkylation with n-propyl bromide and isopropyl bromide at a temperature above 320° also leads to lowering the yield of isopropylbenzene; however at temperature of 340 and 360° it still remains higher by 10-15% than in alkylation with isopropyl alcohol and isopropyl chloride. This difference, evidently, is to be explained by the greater rate of the direct alkylation reaction of benzene with propyl bromide in comparison with the reactions of the decomposition of propyl bromide into propylene and hydrogen bromide and the decomposition of isopropyl bromide into benzene and propylene. Only the fact that the catalytic decomposition of alkylbromides with formation of propylene proceeds more difficultly at higher temperatures than the decomposition of alkylchlorides, and, that the decomposition of the latter proceeds more difficultly than the decomposition of alcohols, is evidence that the direct alkylation reaction (without intermediate formation of unsaturated compounds) is possible. The very yields of isopropylbenzene which we obtain are higher in sum in the alkylation with isopropyl bromide, less in alkylation with isopropyl chloride and still less in alkylation with isopropyl alcohol. In addition, we also obtained direct evidence that alkylation with propyl bromides at temperatures below 260° proceeds without intermediate formation of unsaturated compounds.

We previously noted that during the alkylation of benzene with propylene, a rapid lowering of the activity of the catalyst occurs, and it also becomes slightly active in the alkylation with isopropyl alcohol. The situation is otherwise in alkylation with isopropyl bromide (Table 3).

As is evident from the data of Table 3, the yield of isopropylbenzene in alkylation with isopropyl bromide after passing over the catalyst (10 g), 42.5 g of a mixture of propylene and benzene (experiments 97c and 97d), or 25.4 g of a mixture of propylene and benzene and 24.1 g of a mixture of isopropyl alcohol and benzene, (experiments 98b and 98c) is diminished by a total of 5-8%. In alkylation with the same alcohol, even after passing 20-25 g of a mixture of propylene and benzene, the yield of isopropylbenzene falls by 20-22%. The high yield in the experiments with isopropyl bromide can not be explained by the freeing of the surface of the catalyst from products which cause its deactivation after alkylation with propylene. Evidence concerning this is furnished by the results of experiment 98e, in which the yield of isopropylbenzene is equal in all to 23.2%, i.e., carrying out the alkylation with isopropyl bromide (experiment 98d) does not improve upon the yield in alkylation with isopropyl alcohol.

TABLE 3

Experiment No.	Alkylating Agent	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
97a	iso-C_3H_7Br	25.3	68.2
97b	iso-C_3H_7Br	23.0	66.6
97c	$CH_3CH{=}CH_2$	21.0	29.7
97d	$CH_3CH{=}CH_2$	21.5	21.9
97e	iso-C_3H_7Br	20.5	62.7
98a	iso-C_3H_7Br	25.7	73.0
98b	$CH_3CH{=}CH_2$	25.4	35.0
98c	iso-C_3H_7OH	24.1	26.9
98d	iso-C_3H_7Br	25.2	65.2
98e	iso-C_3H_7OH	25.0	23.2

Note: The temperature was 320°, the rate of supply of the reaction mixture, 0.5 ml/ml per hour and the catalyst 30 ml (10 g).

TABLE 4

Physico Chemical Constants of the Alkylbenzenes Obtained

Alkylbenzene	Boiling point	d_4^{20}	n_D^{20}	MR_D		Molecular weight		M.p. of the acetamido derivatives*	Alkylating agent
				Found	Calc.	Found	Calc.		
Isopropylbenzene	149-151*	0.8634	1.4914	40.3	40.2	122, 124	120	105-105.5	Isopropyl alcohol
Isopropylbenzene	149-151	0.8630	1.4912	40.3	40.2	121, 120	120	105-105.5	n-Propyl alcohol
Isopropylbenzene	148-151	0.8626	1.4912	40.4	40.2	118, 119	120	104-105	Propylene
Isopropylbenzene	149-152	0.8628	1.4915	40.4	40.2	124, 120	120	105.5-106	Isopropyl chloride
Isopropylbenzene	150-153	0.8623	1.4912	40.4	40.2	121, 118	120	104-105	Isopropyl bromide
Isopropylbenzene	149-151	0.8628	0.4910	40.3	40.2	121, 117	120	104.5-105.5	n-Propyl bromide
Ethylbenzene	132-138	0.8701	1.4956	–	–	116, 114	106	225-225.5**	Ethyl alcohol
Ethylbenzene	131-136	0.8694	1.4953	35.6	35.5	106, 108	106	225-225.5**	Ethyl bromide
Tertiary-butylbenzene	162-170	0.8707	1.4879	44.8	44.8	130, 127	134	168-169.5	Tertiary-butyl alcohol
Tertiary-butylbenzene***	160-170	0.8854	1.4863	–	–	128, 126	134	167-168	Isobutyl bromide

* The acetamido derivatives were prepared by the method of Ipatieff and Schmerling [15].

** The melting point presented is that of the diacetamido derivatives.

*** A test (Beilstein's method) showed the presence of halogen.

To explain the high yields of isopropylbenzene in the reaction of isopropyl bromide with benzene after the catalyst appears to a considerable extent poisoned for alkylation with propylene and isopropyl alcohol, the following hypotheses can be proposed:

1) Less activation energy is required for alkylation of benzene with isopropyl bromide than for alkylation

with propylene and isopropyl alcohol, i.e., the first reaction proceeds readily after the deactivation of the most active centers of the catalyst, on which the alkylations of benzene with propylene and alcohol proceed.

2) The alkylation of benzene with propylene and with alcohol, and the alkylation with isopropyl bromide proceed on different kinds of active centers; the transformation products of propylene poison the active centers on which the first two alkylation reactions proceed.

The first hypothesis seems more probable to us. Further research is required for the final solution of this problem.

Identification of the Alkylation Products

The liquid reaction products were distilled in a fractionating column. The constants of the monoalkylbenzenes are presented in Table 4.

In addition to monoalkylbenzenes, diisopropylbenzene was isolated from the combined high-boiling fractions obtained in the experiments with propyl alcohols and propyl bromides:

B. p. 200-206°; d_4^{20} 0.8608; n_D^{20} 1.4910; MR_D 54.6; M 162, 156. $C_6H_4(C_3H_7)_2$.
Calculated: MR_D 54.0; M 162

To determine the position of the propyl groups in the diisopropylbenzene, 2 g of it was acidified by boiling with 20% nitric acid. Terephthalic acid was obtained as a result of the oxidation; this was proved by preparing a dimethyl ester from it which had a m.p. of 140°.

SUMMARY

1. An investigation of the alkylation of benzene with alcohols and halogen derivatives of the fatty series over aluminosilicate catalyst was carried out.

2. It was established that at a molar ratio of benzene to alkylating reagent of 4:1, the reaction products are basically monoalkylbenzenes.

3. The highest yields of alkylation products were obtained in alkylation with propyl alcohols and with propyl halides. Under optimal conditions (temperature 300-320°, a rate of supply of the reaction mixture of 0.25-0.5 ml per ml of catalyst per hour), the yield of propylbenzene amounts in alkylation with isopropyl alcohol to 50-60% of the theoretical, with n-propyl alcohol to 45-58%, with isopropyl chloride to 58-63%, with n-propyl bromide to 67% and with isopropyl bromide to 70-74%. The formation of alkylbenzenes is insignificantly small in alkylation with ethyl, isobutyl and tertiary-butyl alcohols, with ethyl bromide and with isobutyl bromide.

4. Alkylation of benzene with n-propyl alcohol and n-propyl bromide is accompanied by isomerization of the alkyl group and the reaction product is isopropylbenzene. In alkylation with isobutyl bromide, tertiary-butylbenzene is obtained.

5. In alkylation with propylene, the activity of the catalyst is quickly lowered in the course of the experiment. The reduction in catalyst activity in alkylation with alcohols and alkyl halides proceeds considerably more slowly. Catalyst which has been deactivated for alkylation with propylene, is not active for alkylation with alcohols either, but remains active for alkylation with alkyl halides.

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* See Consultants Bureau Translation, p. 937.

KINETICS OF THE HYDROGENATION OF THE BENZYL ESTER OF CINNAMIC ACID ON A POROUS NICKEL CATALYST

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The hydrogenation of the ethylenic bond in the benzyl ester of cinnamic acid has heretofore hardly been studied at all. The hydrogenation of the benzyl ester of cinnamic acid on a Ni catalyst on a silica gel, to which osmium was added, was studied in the work of Sokolsky and Vyugova [1].

In the present work, experimental material pertaining to the study of the influence of the rate of mixing on the rate of hydrogenation of the benzyl ester of cinnamic acid at 0, 25, and 40° is presented. It has been shown that the intensity of mixing during the preliminary saturation of the catalyst with hydrogen plays a decisive role in the formation of the porous nickel catalyst with a standard dispersion; consequently in the study of the dependence of the reaction rate on the rate of mixing, it occurred to us to saturate the catalyst with hydrogen under maximally intense conditions of mixing. Observation of this condition in the preparation of the catalyst permitted the demarcation of the diffusion and kinetic regions of the course of the reaction to be carried out more readily.

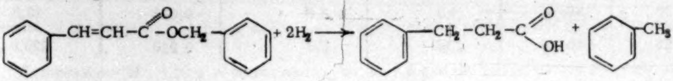
EXPERIMENTAL

The study of the kinetics of the hydrogenation of the benzyl ester of cinnamic acid was carried out with a chemically pure "Kahlbaum" brand preparation with a m.p. of 39° that was in complete agreement with the literature data.

The catalyst was prepared by leaching grains of a Ni - Al alloy with a content of 50% Ni [dimensions of the grains 0.2-0.4 mm (No. 1) or 0.4 - 1 mm (No. 2)] with 20% NaOH on a boiling water bath for 2 hours, after which the catalyst was washed with water and alcohol.

96% Ethyl alcohol was used as the solvent. Electrolytic hydrogen was used for the hydrogenation. The apparatus and experimental methods have previously been described by us [2].

The hydrogenation of the benzyl ester of cinnamic acid in the liquid phase, in all probability, can proceed with the formation of hydrocinnamic acid and toluene according to the following scheme:



To establish the direction of the hydrogenation of the ester on the porous nickel, an experiment was carried out in which a sample of the benzyl ester of cinnamic acid amounted to 60 g. The catalyst was prepared by leaching 15 g of Ni–Al alloy (with a content of 30% Ni).

200 ml of 96% ethyl alcohol and 60 g of ether were added to the catalyst.

The hydrogenation was carried out in a glass vessel, 0.5 liters in volume, at room temperature.

8.8 liters of hydrogen (11.3 liters were necessary according to the calculation) was consumed in the hydrogenation of 60 g of the ester after 675 minutes, after which the experiment was discontinued. After completion of the experiment, the catalyst was filtered off. The catalyzate in ethyl alcohol solution had the characteristic odor of toluene. Upon addition of bromine water to a portion of the catalyzate (2-3 ml), the bromine water was not decolorized, which indicated the absence of an unsaturated bond. The constant-boiling mixture of alcohol and toluene, 215 ml of which was formed as a result of the hydrogenolysis, was then distilled off.

100 ml of water was added to the same quantity of this mixture; the mixture was then intensively extracted. After separating the two layers the upper layer was dried over $CaCl_2$ and fractionated. 6 ml of toluene was thereby obtained. Thus, $6 \cdot 2.15 = 12.9$ ml of toluene can be isolated from 215 ml of the mixture, which corresponds (according to the hydrogen consumption) to the calculated quantity of toluene. Water was added to the residue in the distillation flask (evidently, a mixture of hydrocinnamic acid and the benzyl ester of hydrocinnamic acid) and the mixture was heated to 100°. Hydrocinnamic acid was isolated from the solution, and after washing with cold water and drying, was characterized by a m.p. of 48.5°, which is in accord with the literature data for hydrocinnamic acid and confirms the reaction course indicated by us.

The kinetics of the hydrogenation of the ester at various temperatures was studied in subsequent experiments. The kinetic hydrogenation curves and the results of these experiments are presented in Fig. 1 and Table 1.

As is evident from curve I (Fig. 1), the hydrogenation of the ester at 0° proceeds almost as a first order reaction, , and the reactions , with an absorption of hydrogen of 62% of the theoretical, necessarily proceed at immeasurably slow rates. This inhibition of the reaction is apparently caused by the formation of the benzyl ester of hydrocinnamic acid, which is slightly soluble under these conditions and blocks the active nickel surface. Experiments carried out at 25° (curves II and III), showed that the hydrogenation of the ester was a mixed order reaction. Up to the absorption of 56.0% of the theoretical quantity of hydrogen, the order of the reaction is necessarily fractional (convex curves) and then, on further absorption of hydrogen, the curves acquire a linear character. In almost all cases, the reaction does not proceed to conclusion, since it proceeds for a long time at immeasurably small rates.

In our case, a certain selectivity of the process on the porous nickel at 25° is evidence of the mixed order of the reaction. It can doubtless be considered that the hydrogenation of the $-CH=CH-$ bond in the benzyl ester of cinnamic acid proceeds initially. The results of hydrogenation of a 60 g sample of the ester also lead to this conclusion; in the given case, the presence of the $-CH=CH-$ bond was not detected (with bromine water) after the absorption of 77% of the theoretically necessary hydrogen.

TABLE 1

Influence of the Temperature on the Rate of Hydrogenation of the Benzyl Ester of Cinnamic Acid on Porous Nickel

0.56 g of porous nickel (No. 2); 0.5 g of the ester; 25 ~~ml of~~ 96% alcohol. The catalyst was preliminarily saturated with H_2 for 15 min. The rate of mixing was 840 rocking oscillations per minute.

Experiment No.	Temperature	Order of the reaction	1/2 V_0 H_2 after t minutes	$(\Delta V_0/\Delta t)_{av}$ up to the absorption of 1/2 V_0 H_2	K_t for hydrogenolysis	Quantity of H_2 absorbed in the hydrogenation (ml)
150	0°	First	36.0	1.3	–	58.0
128	25	Mixed	10.0	4.7	0.016	82.4
129*	25	Mixed	10.0	4.7	0.016	83.1
135	40	Mixed	7.0	6.6	0.041	84.6
145	50	Mixed	7.0	6.6	0.036	85.0
136**	25	Mixed	23.5	6.0	0.010	220.0

* Repetition of experiment 128

** The ester sample weighed 1.5 g.

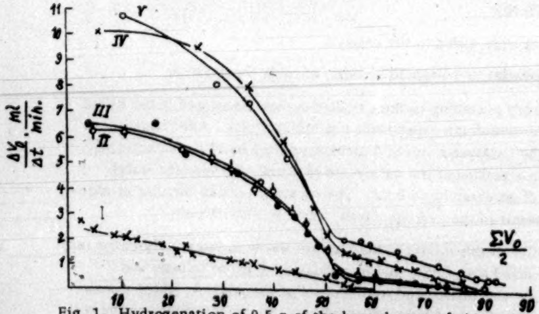


Fig. 1. Hydrogenation of 0.5 g of the benzyl ester of cinnamic acid at various temperatures. Explanation in the text.

The order of the reaction was not changed by raising the temperature to 40-50° (Fig. 1, curves IV and V). This circumstance indicated that the selectivity of the hydrogenation of the ester within the limits studied by us did not depend on the temperature. It follows that rate of hydrogenation of the $-HC=CH-$ bond is characterized by the time for half-hydrogenation and the average rate, while the hydrogenolysis is characterized by the rate constant of a first order reaction.

As is evident from the data of Table 1, raising the temperature to 50° does not lead to increase in the rate of the first process and even rather delays the second. The rate constant of hydrogenolysis at 50° was equal to 0.036. In addition, at 50° a considerable scattering of points is observed on the kinetic curve (curve V).

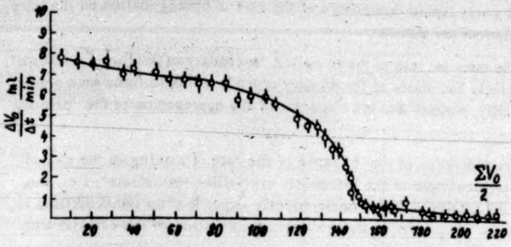


Fig. 2. Hydrogenation of 1.5 g of the benzyl ester of cinnamic acid.

The kinetic curve for the hydrogenation of a three-fold sample (1.5 g) of the ester of cinnamic acid at 25° (Table 1, experiment 136) is presented in Fig. 2. The kinetics of the reaction also correspond to that of a mixed order reaction in this case. Increase in the concentration of the hydrogenated substance leads to some increase in the rate of hydrogenation of the −CH = CH − bond, which is characteristic for a fractional order reaction in an unsaturated compound. The rate constant of the hydrogenolysis with increase from 0.5 to 1.5 g in the sample of the substance being hydrogenated on the average remains constant and equal to 0.01.

In subsequent experiments we studied the dependence of the rate of hydrogenation of the benzyl ester of cinnamic acid on the rate at which the reaction mixture was shaken. With this object, two series of experiments were conducted. In the first series, preliminary saturation of the catalyst with hydrogen was carried out at the same intensity of mixing as in the hydrogenation; in the second series, the preliminary saturation of the catalyst with hydrogen was brought about with a maximum intensity of shaking. The results of these experiments are shown in Table 2 and Fig. 3.

The results presented in Table 2 show that with increased intensity of shaking in the range from 540 to 1340 rocking oscillations per minute during both the preliminary saturation of the catalyst with hydrogen and during the hydrogenation, a steady increase in the reaction rate occurs. As regards the hydrogenolysis constant, it remains almost constant both at small, and at considerable rates of mixing (within the limits studied by us) and is equal in the first case to 0.025 and in the second to 0.020. This phenomenon, apparently, is caused by sufficient dispersion of the catalyst in the process of hydrogenation of the −CH = CH − bond.

TABLE 2

Influence of the Intensity of Mixing on the Rate of Hydrogenation of the Benzyl Ester of Cinnamic Acid

Temperature 25°; 0.56 g of porous nickel (No. 2); 0.5 g of the benzyl ester of cinnamic acid; 25 ml of 96% alcohol. The preliminary saturation of the catalyst with hydrogen was carried out for 15-20 minutes. The order of the reaction was mixed in all cases.

Experiment No.	Rate of shaking during the preliminary saturation of the catalyst (number of rocking oscillations per minute)	Number of rocking oscillations per minute during the hydrogenation.	Half hydrogenation time ([illegible] (minutes)	$(\Delta V_0 / \Delta_t)_{av.}$ up to the absorption of 1/2 V_0 H_2	$K_{25°}$ for hydrogenolysis
201*	216	216	11.0	4.3	0.030
202*	250	250	11.0	4.3	0.020
203*	320	320	10.0	4.7	0.026
204*	400	400	9.5	5.0	0.025
144	540	540	16.0	2.9	0.020
140	680	680	16.0	2.9	0.017
128	840	840	10.0	4.7	0.020
129**	840	840	10.0	4.7	0.020
141	1070	1070	9.5	4.9	0.020
142	1220	1220	8.0	5.9	0.021
143	1340	1340	8.0	5.9	0.020

* The experiments were carried out with porous Ni (No. 1), prepared from a 50% very finely ground alloy (powder type).

** Repetition of experiment 128

In this connection, it is curious that experiments Nos. 201-204, carried out with porous nickel from a very finely divided alloy (powder type), exhibited a very feeble dependence of the rate of hydrogenation on the intensity of mixing (from 216 to 400 rocking oscillations per minute).

In the aggregate, these data indicate the essential role of the so-called "secondary crystalline formations", which, as Rubinshtein [3] showed, consist of blocks and druses of the primary crystals and determine such properties of the catalyst as its specific surface, density, porosity and the character of the aggregation of the "primary crystals".

In connection with the question under consideration of the influence of the rate of mixing on the rate of hydrogenation, it is impossible to ignore the physical state of the "secondary crystalline formations", i.e., the dispersion of the catalyst. The dispersion of the catalyst is undoubtedly directly dependent on the conditions of the stirring; consequently varying intensity of the mixing during the preliminary saturation of the catalyst with hydrogen creates irregular conditions for the genesis of the porous nickel.

In this connection it was of interest to study the influence of the rate of mixing on the rate of hydrogenation of the ester with a strictly standard catalyst. This study was carried out at 0, 25, and 40°. In these experiments the preliminary saturation of the catalyst with hydrogen was carried out with a greater intensity of the shaking of the "duck" (1080 rocking oscillations per minute). The intensity of the shaking of the reaction mixture during the hydrogenation varied from 200 to 1320 rocking oscillations of the "duck" per minute. The experimental data are presented in Fig. 3.

In comparing the experimental results presented in Table 2, with the results presented in Fig. 3, it is not difficult to note the substantial influence of the rate of the mixing during the preliminary saturation of the catalyst with hydrogen on the rate of hydrogenation of the ester.

It is not possible to set a boundary for the conversion of the "diffusion" region into the "kinetic" region from the data of the first series of experiments (Table 2).

The dispersion of the catalyst is constant under conditions of maximum intensity of shaking of the mixture during the preliminary saturation of the catalyst with hydrogen (Fig. 3). This circumstance permits the demarcation of the regions of the reaction to be carried out graphically; if the process is carried out in the "kinetic" region, the reaction rate is characterized by a constant value.

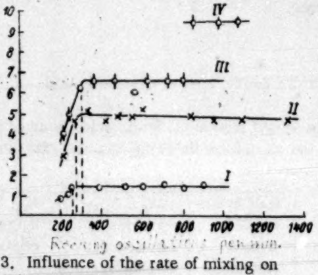


Fig. 3. Influence of the rate of mixing on the rate of hydrogenation of the benzyl ester of cinnamic acid at various temperatures. I) 0° II) 25° III) 40° IV). 40° (Ni No. 2).

The hydrogenolysis constant does not depend on the rate of mixing in the ranges studied by us and corresponds at a temperature of 25° to a value of 0.016 and at 40°, to 0.040. The apparent activation energy of the hydrogenolysis in this temperature range proved to be equal to 13950 cal/mole.

The position of the transition boundary of the "diffusion" region into the "kinetic" region depending on the temperature is noteworthy. As the curves show (Fig. 3), this transition is brought about at greater rates of stirring at higher temperatures. Thus, at 0° the transition boundary is found at about 250, at 25°, at around 270, and at 40°, at around 300 rocking oscillations per minute.

We also found a similar rule in the hydrogenation of dimethylacetylenylcarbinol [2]; this is completely explicable if one takes account of the fact that the temperature coefficient of the reaction is considerably higher than the temperature coefficient of diffusion. The difference in the temperature coefficients in the "diffusion" and in the "kinetic" regions was shown in the case of sunflower oil in the work of Elovich and Zhabrova [4].

The data presented in Fig. 3, permit the calculation by the Arrhenius formula of the apparent activation energy in the "diffusion" and "kinetic" regions. The results of these calculations are placed in Table 3.

It is evident from the data of Table 3, that at a comparatively low temperature, (0 - 25°), both in the "diffusion" and in the "kinetic" regions, the temperature coefficient is considerable and the value of the apparent activation energy corresponding to it is 6880 cal/mole in the "diffusion" region and 7960 cal/mole in the kinetic region. At higher temperatures (25-40°) the temperature coefficient has a lower value both in the "diffusion" and in the "kinetic" regions; the apparent activation energy in the "diffusion" region is characterized by a value of 3900 cal/mole and in the "kinetic", by 4400 cal/mole.

TABLE 3

Reaction region and rate of mixing	$(\Delta V_0/\Delta_\tau)_{av.}$ (in ml/minute) up to the absorption of 1/2 V_0 H_2 at the given temperature				Apparent activation energy (± 500 cal/mole) in the given temperature range		
	0°	25°	40°	50°	0-25°	25-40°	40-50°
Diffusion region, 210 rocking oscillations per minute	0.9	2.9	4.5	–	6880	3900	–
Kinetic region, 800 rocking oscillations per minute	1.4	4.8	6.7	6.7	7960	4400	0

The activation energy for hydrogenation of the $-CH=CH-$ bond, calculated in the temperature range 40-50° (in the "kinetic" region), is equal to zero.

The diminution of the temperature coefficient of the reaction may be a result of the fact that with increase in temperature, the ratio of concentrations of the reacting components changes at the surface of the catalyst. To confirm this, it would be necessary to use the potentiometric method of investigation which makes it possible to measure accurately the concentration of one of the reacting substances on a surface [5].

SUMMARY

1. It was established that the hydrogenation of the benzyl ester of cinnamic acid proceeds with rupture of the O–C bond at room temperature on porous nickel, and the reaction products are toluene and hydrocinnamic acid.

2. It was shown that the rate of hydrogenation of the ester up to the absorption of 56% of the theoretical quantity of hydrogen is comparatively great – under these conditions the hydrogenation of the $-CH=CH-$ bond proceeds; hydrogenolysis proceeds at low rates.

3. The influence of the rate of mixing on the rate of hydrogenation of the ester at 0, 25, and 40° was studied. It was shown that the intensity of mixing in the preliminary saturation of the catalyst with hydrogen plays a decisive role in the genesis of the catalyst.

4. With the use of the mixing factor, demarcation of the "diffusion" and "kinetic" regions of hydrogenation of the $-CH=CH-$ bond at various temperatures was carried out. It was established that the hydrogenolysis constant at 25 and 40° does not depend on the rate of stirring (in the limits of 200 - 1320 rocking oscillations per minute of the "duck"). At low temperatures (0 and 25°), there are high values for the activation energy (7-8 kcal/mole) in both regions of hydrogenation of the $-CH=CH-$ bond. At high temperatures (from 25 to 50°), the temperature coefficient of hydrogenation of the $-CH=CH-$ bond is insignificant and the apparent activation energy diminishes to zero.

The apparent hydrogenolysis energy in the 25-40° temperature range is equal to 13950 cal/mole.

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S. M. Kirov Kazakh State University

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TABLE 5

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The activation energy for [illegible] equal to [illegible]

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MERCAPTANS AND DISULFIDES AS CHAIN TRANSFER AGENTS IN THE THERMAL POLYMERIZATION OF STYRENE

V. A. Dinaburg and A. A. Vansheidt

In the chain polymerization of vinyl compounds, initiated by free radicals, along with the three basic reactions – the formation of active centers, the growth of chains and their inactivation – so-called chain transfer reactions often occur which lead to a more or less marked lowering in the molecular weight of the polymer obtained without lowering the over-all rate of the polymerization.

These reactions ordinarily proceed during the polymerization of vinyl compounds in the presence of organic solvents which contain hydrogen or halogen and proceed particularly readily in the presence of alkylmercaptans. The latter are often used in technology under the name of regulators or modifiers, since even insignificant additions of these substances to a monomer are capable of evoking marked change in the molecular weight and properties of the end products of the reaction.

In the process of chain transfer there usually occurs the breaking away by the growing chain $RM_n^{\cdot}$ of an atom of halogen or hydrogen (X) or of regulator XY, with simultaneous formation of a new free radical $Y\cdot$, which, reacting with the monomer, yields the beginning of a new growing chain $YM_n^{\cdot}$. Consequently, in spite of the frequent breaking off of chains, the reaction is not terminated and, as a result of the repeated transfer of chains, polymer molecules are formed, the ends of which are mostly saturated with X and Y radicals.

The kinetics of these reactions was studied for the first time by Kamensky and Medvedev [1] in the case of polymerization of vinylacetate in benzene solution and by Medvedev, Koritskaya and Alekseeva [2] in the case of polymerization of styrene in the presence of benzene, its homologs and cyclohexane.

On the other hand, Mayo [3] indicated that at a low polymerization the dependence $\frac{1}{P} = \frac{1}{P_0} + \frac{[S]}{[M]}$ applies, where p_0 and p are the degrees of polymerization of the polymer obtained in the absence of regulator, and at a molar ratio of regulator to monomer equal to $[S] / [M]$.

Consequently, quantities which are the reciprocals of the average extent of polymerization (1/p) of the polymer obtained, are linear functions of the ratio [S]/[M] and depend on a certain constant C, which Mayo called the transfer constant of the chain, and is equal to the ratio of the rate constants of the reactions of transfer and of growth of the chains. Thus the constant C characterizes the degree of activity of the solvent as an agent of chain transfer.

This constant was determined by Mayo [4] for a number of hydrocarbons and their halogen derivatives, and it turned out that with increasing mobility of the hydrogen in the hydrocarbons, it increased, for example in progressing from benzene to fluorine (at 100°) from $1.84 \cdot 10^{5}$ to $1.24 \cdot 10^{-2}$, i.e., by almost 700 times. At 100°, carbon tetrachloride proved to be 1000 times more active than benzene. As regards the mercaptans, the constants for only a few of them are given in the literature, specifically for 4-alkylmercaptans [5,6,8], 3-ethoxypropanthiol and the ethyl ester of thioglycolic acid [5]. Their magnitude (at 60°) reaches 3.8 for tertiary-butylmercaptan and 20.0 for primary alkylmercaptans, i.e., it exceeds the constant for benzene at 60° ($0.18 \cdot 10^{-5}$) by a million times.

The great activity of mercaptans can be explained by the greater mobility of the hydrogen of the SH groups in them, which, as a consequence of this, is readily torn off by the growing radicals with simultaneous formation of $RS\cdot$ radicals which initiate the growth of new chains. Consequently, the end products of polymerization in these cases are polymers of the composition $RS(C_8H_8)_nH$, which was confirmed by their analysis [7,9].

As regards information of chain transfer by disulfides, such information is still limited to the data of Snyder [7] on the polymerization of styrene in the presence of diisopropylxanthogendisulfide, which proved to be a rather strong chain transfer agent. However its chain transfer constant was not determined, any more than the chain transfer constants of other disulfides, although it can be assumed that, as a consequence of the instability of the S–S bond, the capacity to transfer chains by the following scheme should be more or less inherent in all of them:

$$RM_n\cdot + R'S{-}SR' \longrightarrow RM_nSR' + R'S\cdot$$

$$R'S\cdot + nM \longrightarrow R'SM_n^{\cdot}$$

The material published in the literature does not permit one to judge whether, to what extent and in which directions the nature of the radical in compounds of the RSH and RSSR type influences their activity in the process of chain transfer, i.e., on their capacity to enter into reaction with growing chains, with the formation of new free radicals.

Consequently, we synthesized a number of mercaptans and disulfides which contain various fatty, fatty-aromatic, aromatic and heterocyclic radicals and determined their chain transfer constants in the process of thermopolymerization of styrene at 100° in the absence of oxygen. The constants were determined by Mayo's method in the majority of cases (when their magnitude did not exceed 5.0), i.e., via the determination of the average molecular weights of the polymers obtained in the presence of various quantities of regulator at low polymerization. However, in the case of the highly active mercaptans, this method, as a consequence of the rapid consumption of mercaptan even in the initial stages of polymerization, did not yield correct results. Consequently in these cases we used (where this was possible) another method of determining the chain transfer constant, which was based on the determination of the quantity of polymer formed and of unreacted mercaptan remaining in the process of polymerization of styrene [8].

The results of these experiments are set forth in Tables 1 and 2, from which it is evident that the chain transfer constants of the compounds which were investigated vary within very wide limits, specifically from 0.0045 to 28.0.

It follows from Table 1, that all the primary alkylmercaptans and their derivatives which contain the CH_2SH group are characterized by great magnitudes of the constants of the order of 15.0 and more, and, thus, are powerful chain transfer agents, while the secondary octylmercaptan with $C = 3.2$ is considerably less active. A similar difference in activity between primary and tertiary mercaptans was found by Gregg, Aldermann and Mayo [5] in the case of the primary dodecylmercaptan ($c = 18.7$ at 60°) and tertiary-butylmercaptan ($C = 3.6$). Thus, the occurrence of the SH group in the middle of the chain markedly lowers the activity of the mercaptan. However, lengthening the chain hardly influences the degree of the activity of primary mercaptans, as the table shows. However, the introduction of the COOR group in the alpha position to the SH group considerably increases the activity of the mercaptan. This is evident in the case of the methyl ester of thioglycolic acid investigated by us ($C = 27.6$) and also from the data of the authors named above for the ethyl ester of the same acid ($C = 58$ at 60°).

We succeeded in determining the constant of thioglycolic acid itself ($C > 14$) only by a viscosimetric method and its true value must be at least twice as large as was observed for the ester of this acid. It is evident from this, that the carboxyl group, found in the alpha position to an SH group, increases the activity of the latter no less strongly than the $COOCH_3$ group.

TABLE 1

Chain Transfer Constants of Aliphatic and Aliphatic-Aromatic Mercaptans and Disulfides

R	RSH	RSSR
CH_3CH_2-	–	0.0045
$CH_3(CH_2)_2CH_2-$	15.4	0.0068
$CH_3(CH_2)_4CH_2-$	15.3	0.0104
$CH_3(CH_2)_5CH_2-$	15.1	–
$CH_3(CH_2)_{16}CH_2-$	14.7	0.024
$CH_3(CH_2)_5CHCH_3$	3.2	0.0104
$C_6H_5-CH_2-$	25.5	0.011
p-$CH_3OC_6H_4CH_2$	26.0	0.021
α-$C_{10}H_7-CH_2-$	24.6	0.033
$-CH_2COOH$	> 14.0 *	0.20
$-CH_2COOCH_3$	27.6	0.10
CH_3CO-	> 14.7 *	–
C_6H_5CO-	> 6.23 *	0.11
$(CH_3)_2OCHCSS-$	–	> 7.5 *

* The constants were determined viscosimetrically and therefore are less than the true values.

Analogous considerations force us to assume that the constant of the thioacetic acid ($C > 14.7$) is actually considerably higher, i.e., that the CH_3CO- group, directly bound to the SH group, also markedly activates the latter.

As regards the disulfides, as is evident from Table 1, they are a hundred and even a thousand times less active than the corresponding mercaptans. Thus, for example, in proceeding from n-butylmercaptan to dibutyldisulfide, the chain transfer constant is diminished by 2250 times. However, as the chain is elongated (from C_2 to C_{18}) the constants of the disulfides visibly increase (from 0.0045 to 0.024), as a consequence of which the difference in the degree of activity of mercaptans and disulfides is diminished.

A still greater increase in the activity of the disulfides is observed under the influence of the COOR group, as is evident in the case of the dithiodiglycolic acid (C = 0.2) and its ester (C = 0.1).

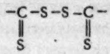
This is evidence that lengthening the chain, and also introduction into the chain of a carboxyl group in the alpha position, reduces the strength of the S–S bond in disulfides.

As regards the influence of the introduction of aromatic nuclei into alkylmercaptans and disulfides in the alpha position, as is evident from Table 1, in the mercaptans it is expressed as a 1.7 - 1.8-fold increase in the activity of the primary alkylmercaptans, but has little influence on the activity of the disulfides. For example, primary dihexyldisulfide and dibenzyldisulfide hardly differ from each other in the magnitude of the constant. However, replacement of the phenyl group in the latter by the β- naphthyl group increases the constant to 0.03, evidently also as a consequence of weakening of the S–S bond.

Judging by the magnitude of the chain transfer constant, this bond is still more weakened in dibenzoyldisulfide which is analogous to benzoyl peroxide but in contrast to the latter, dibenzoyldisulfide hardly accelerates the polymerization of styrene at all.

Thus, although the bond between atoms of sulfur and dibenzoyldisulfide is somewhat weakened, it is nevertheless comparatively strong.

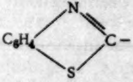
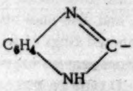
On the other hand, although diisopropyldixanthogendisulfide also has slight influence on the rate of polymerization of styrene, the constant found for it viscosimetrically is C = 7.5, which must actually be still larger and markedly differs in its exceptionally large magnitude from the constant of the other disulfides which, evidently, is to be explained by the presence in this disulfide of the very unstable grouping



$-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-$.

TABLE 2

Aromatic and Heterocyclic Mercaptans and Disulfides

R	RSH		RS–SR	
	% of the polymer	C	% of the polymer	C
C_6H_5-	7-12	0.08	3.7	0.14
$-CH_3C_6H_4-$	14-16	0.07	4.5	0.15
β-$C_{10}H_7-$	10	0.18	4.0	0.36
α-$C_{10}H_7-$	9-16	0.15	4.2	1.57
p-$C_2H_5OC_6H_4-$	11-13	0.13	3.7	0.33
o-$C_2H_5OC_6H_4-$	3.5	25.1	4.2	0.075
o-$HOCOC_6H_4-$	3.5	<14.7	–	–
o-$CH_3OCOC_6H_4-$	3.0	17.0	4.0	0.20
	4.0	0.26	3.5	2.73
	4.3	0.21	–	–

In proceeding to the aromatic and heterocyclic mercaptans and disulfides, which are characterized by the presence of a direct bond of the sulfur atoms with the aromatic nuclei or heterocyclic rings, the marked difference of the constants of many representatives of these groups of compounds from those of the aliphatic and aliphatic-aromatic compounds should be noted.

The chain transfer constants of these compounds and the average polymer yields obtained in their presence are compared in Table 2.

The mercaptans of this type are characterized in the majority of cases by very low chain transfer constants, which vary from 0.07 to 0.26. Thus, in their activity they are 100-200 times less than the primary and 25-30 times less than the secondary and tertiary alkylmercaptans. This group includes thiophenol, thio-p-cresol, p-ethoxy-thiophenol and α- and β-thionaphthols and also 2-mercaptobenzthiazole and 2-mercaptobenzmidazole. At the same time it should be noted, that thiophenol and its para-substituted derivatives, and also thionaphthols, cause an increase in the yields of polystyrene from 3.5-4.0 to 7–16%, i.e., a 2–4-fold acceleration of the polymerization, possible as a consequence of their autooxidation with formation of peroxides [13,14]. However, the ortho-substituted derivatives of thiophenol, which contain oxygen as a substituent, such as, for example, o-ethoxythiophenol, thiosalicylic acid and its methyl ester, are distinguished by high constants of the order of 17.0–25.0, i.e., are not second to primary alkylmercaptans in their activity. However, in contrast to the thiophenols and their para-substituted derivatives, they are incapable of accelerating the polymerization of styrene.

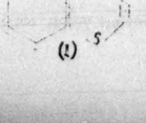
As regards the disulfides which correspond to the mercaptans indicated above, they all had comparatively high constants, the magnitude of which varied from 0.14 to 2.7, as a consequence of which the disulfides under consideration (with the exception of the ortho-substituted compounds) proved to be 2–10 times more active than the corresponding mercaptans.

The increasing activity of the aromatic disulfides, which rises from the phenyl derivatives through the β-naphthyl to the α-naphthyl and benzthiazolylic disulfides can be explained as a weakening of the S–S bond under the influence of unsaturated radicals adjacent to the sulfur atoms similarly to what is observed more clearly with the central C–C bond of hexaarylethanes, which undergoes rupture with formation of free radicals merely as a result of entering into solution. However, judging by the fact that these disulfides do not substantially change the rate of polymerization of styrene even at large chain transfer constants of the order of 2.0, the rupture of their S–S bond under the conditions of the polymerization is evidently accomplished only due to their reaction with the growing chains, and the ArS· radicals formed from them are sufficiently active to cause the formation of new chains.

The low activity of thiophenols, thionaphthols and heterocyclic mercaptans, is possibly associated with the presence in them of the C=C–SH and N=C–SH groups, which are distinguished by an increased acidity and a tendency to split off hydrogen in the form of a proton and not of an atom, as is required for the chain transfer mechanism. The increased activity of the aliphato-aromatic mercaptans of the $ArCH_2SH$ type in comparison with alkylmercaptans can, on the contrary, be explained by the lowered degree of their acidity under the influence of aryl groups, since it is well known that replacement of the hydrogen of the CH_3 group by aryl groups increases the basic properties of the carbinol. The marked increase in the chain transfer constant in passing from thiophenol and its para-substituted derivatives to oxygen-containing ortho derivatives is, however, most unexpected.

In this connection, a particularly significant example is that of the isomeric ethoxythiophenols, of which the para-isomer is distinguished by a very low activity (C = 0.13), while the ortho-isomer, on the contrary, is remarkably active (C = 25.4). However, the high activity of other compounds which contain oxygen in positions 5 and 6 relative to the hydrogen of the SH group, for example, thiosalicylic and thioglycolic acids and their esters (C = 17 and 28) is also very significant.

The high activity of all these compounds, apparently, is caused by their cyclization due to the formation of intramolecular hydrogen bonds of the S–H. . . O type. The formation of hydrogen bonds in the case of oxygen analogs of these compounds, for example, salicylic acid and guaiacol, has long been known and demonstrated by various methods. As regards the mercaptans, their properties give no basis for assuming the presence in them of hydrogen bonds of the S–H. . . S type; these bonds can not arise in the given case due to the insufficient electronegativity of sulfur. However, there are data which indicate the possibility of the formation of intermolecular S–H. . . O bonds in solutions of mercaptans in ethers [15]. There are, therefore, grounds for assuming that such bonds arise within the molecules, in particular, if their formation leads to the formation of stable 5- and 6-membered rings. In particular, theory would lead one to expect the possibility of the formation of such rings in the case of the afore-mentioned o-ethoxythiophenol (I), thiosalicylic acid and its esters (II) and thioglycolic acid and its esters (III), and also does not exclude the possibility of the formation in the case of thioacetic and thiobenzoic acids of 8-membered rings of a type (IV), analogous to that which is assumed in the case of carboxylic acids. However, these assumptions require experimental confirmation and the problem of the activating influence of hydrogen bonds of the S–H. . .O type on the capacity of mercaptans to transfer chains is still unsettled.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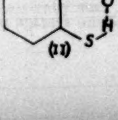
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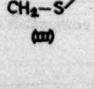
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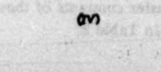
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EXPERIMENTAL

We prepared 22 mercaptans and 20 disulfides (Tables 1,2). They were all isolated in the pure form and had the constants indicated in the literature.

The initial styrene was subjected to careful purification, dried and vacuum distilled before use. On heating to 99° in sealed ampoules in the absence of air, it was 3.5% polymerized after 2 hours, i.e., the normal rate of polymerization [10] was detected which is indicated for the absence of inhibitors or accelerators.

To determine the chain transfer constants, precisely weighed samples of the mercaptan or disulfide were dissolved in 5 g of styrene in 10 to 20 ml ampoules of standard form which were washed, steamed and dried before the experiment. They had two inlet tubes in the upper portion – to charge the reagents and to connect the system with a vacuum. The first inlet tube was sealed after charging. To prevent the influence of oxygen, air was eliminated from the ampoule by carefully displacing it with nitrogen purified from oxygen and evacuating it to a vacuum of 2 mm, whereupon the styrene solution was congealed with dry ice. After repeating the operation of filling with nitrogen and evacuating for 3 or 4 times, the ampoules were sealed in a vacuum and heated in a thermostat and 99 ± 0.5° for 2 hours, after which they were quickly cooled with water and opened. With the object of determining the yield of polymer (it did not ordinarily exceed 5%) a sample was taken from the solution to find the coefficient of refraction. The content of polymer in the solution was calculated by the formula [8]: % polymer = $1.73 \cdot 10^3 \cdot \Delta n_D^{20}$, where Δn_D^{20} is the difference between the coefficient of refraction of the solution before and after polymerization; As the experiments showed, the yield of polymer determined in this way coincided with the yield found by weighing the polymer precipitated from methanol solution.

To determine the molecular weight of the polymers, the latter were precipitated from a solution of a 5-fold quantity of methanol and dried in a vacuum at 80° to constant weight. The specific viscosity of their benzene solutions was then determined at 20° at various polymer concentrations, and in all cases a linear dependence of the quantity $\eta_{sp.} / c$ on the concentration c was observed.

The characteristic viscosity $[\eta]$ was found by graphic extrapolation of the quantity $\eta_{sp.} / c$ to zero concentration. The average numerical molecular weight of the polymers was calculated by the formula $M_n = 184000\ [\eta]^{1.4}$ introduced by Gregg and Mayo [11] for polystyrenes obtained in the polymerization of styrene in the presence of carbon tetrachloride at low percentages of conversion.

With the object of finding the chain transfer constants which characterize the sulfur compounds under study, the polymerization of styrene was carried out at 3 or 4 different concentrations of each compound, and depending on the degree of activity of the latter, the molar ratio of reagents $[XY] / [M]$ was varied within limits of from 0.0001 to 0.016 moles of the substance under investigation per mole of styrene.

The experiments showed that all the mercaptans and disulfides investigated by us to a greater or lesser extent lowered the average degree of polymerization (p) of the polystyrenes obtained in their presence, while the magnitudes of $1/p$ increased linearly in accord with the Mayo equation with increase in the ratio $[XY] / [M]$. This dependence is expressed by straight lines for various compounds which intersect at the point $1/p_0$, corresponding to the value of $1/p$ for pure styrene, but which have varying inclinations as a consequence of the varying degree of activity of the compounds taken.

The chain transfer constants (C) were calculated from these data by the Mayo formula, on the assumption that at an insignificant depth of polymerization the ratio of the reagents in the polymerization process remains practically constant. However, in the case of highly active mercaptans with $C \geq 5$, the constants obtained by this method, as a consequence of the rapid consumption of the mercaptan, remained considerably lower than the true values. In these cases the constants (C) of the mercaptans were also determined by us by titration of the amount of mercaptan which was not consumed in the polymerization at various degrees of conversion of the monomer into the polymer [8].

We accomplished the quantitative determination of mercaptans in the solution by the method of Kolthoff and Harris [12], i.e., by the amperometric titration of mercaptan with silver nitrate in the presence of ammonia. With this object the solution of the mercaptan in styrene was heated in sealed ampoules at 99° for various lengths of time, after which an exactly weighed sample of the polymerizate was diluted with methyl or ethyl alcohol, the polymer was filtered off and washed with alcohol, and the mercaptan was determined in the filtrate by the method indicated above.

The constants, found by this method, were calculated according to the formula:

$$C = \frac{2 - \log \%\,(RSH)}{2 - \log \%\,(M)}$$

where % (RSH) and % (M) are the quantites of unreacted substances (mercaptan and monomer), expressed in percentages of the initial quantities.

The experimental data, on the basis of which the average values indicated in Tables 1 and 2 for the chain transfer constants of the mercaptans and disulfides studied by us in the styrene polymerization process were calculated, are presented in Tables 3 and 4.

TABLE 3

Type of regulator	R–SH				R–S–S–R			
R	% RSH	Time (min).	% of polymer	RSH remaining in % of the original	$\frac{[R_2S_2]}{[M]} \cdot 10^3$	% of polymer	$[\eta]$	$\frac{1}{P} \cdot 10^3$
$CH_3(CH_2)_3-$	0,29	60	1,56	78,2	4,16	3,5	1,904	0,229
		120	3,63	56,9	8,33	3,8	1,744	0,259
		180	5,00	45,2	16.7	3,8	1,536	0,310
$CH_3(CH_2)_5$	0,38	60	2,25	70,1	4,16	4,0	1,772	0,254
		180	5,20	44,0	8,33	4,0	1,634	0,284
		240	6,92	34,0	16,7	4,3	1,376	0,362
$CH_3(CH_2)_6-$	0,42	35	1,73	76,8	4,16*	3,6	1,980	0,217
		240	7,27	33,2	8,33	3,5	1,884	0,233
		360	9,17	23,3	16,7	4,0	1,644	0,280
$CH_3(CH_2)_{17}-$	0,89	20	1,38	82,4	4,16	4,0	1,590	0,295
		120	3,63	56,2	8,33	4,5	1,280	0,400
		180	5,36	44,6	16.7	5,4	0,967	0,592
$CH_3(CH_2)_5\overset{\mid}{C}HCH_3$	0,46	120	3,46	90,2	4,16	3,5	1,762	0,256
		180	5,0	83,1	8,33	3,6	1,634	0,285
		240	6,9	82,1	16,7	3,8	1,368	0,365
CH_3OCOCH_2-	0,32	120	3,46	37,5	4,16	3,6	0,920	0,630
		180	5,19	23,2	8,33	3,8	0,626	1,090
		240	6,23	17,0	16,7	4,0	0.438	1,800
$C_6H_5CH_2-$	0,39	60	2,08	58,9	4,16	3,8	1,770	0,254
		180	5,71	22,2	8,33	3,8	1,604	0,292
		240	7,44	13,7	16,7	4,5	1,314	0,386
$p-CH_3OC_6H_4CH_2-$	0,46	60	1,21	70,5	2,08	4,1	1,770	0,254
		120	3,1	46,3	4,16	4,0	1,638	0,283
		180	5,2	25,6	8,33	4,5	1,360	0,368
$\alpha-C_{10}H_7CH_2-$	0,55	60	2,9	48,4	2,08	3,8	1,656	0,280
		120	7,6	14,2	4,16	3,6	1,444	0,340
		240	9,9	7,6	8,33	3,5	1,150	0,470
$o-C_2H_5OC_6H_4-$	0,62	60	2,4	55,0	2,08	3,8	1,360	0,367
		120	3,5	40,0	4,16	4,0	1,082	0,506
		180	5,4	24,4	8,33	4,5	0,775	0,808
$o-CH_3OCOC_6H_4-$		120	2,8	62,9	1,04	3,8	1,940	0,223
		180	4,15	49,3	2,08	4,5	1,826	0,243
		240	6,4	31,7	4,16	4,3	1,648	0,281

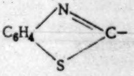
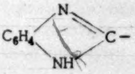
* $R=C_2H_5$

SUMMARY

1. The thermopolymerization of styrene at 99° in the presence of 22 mercaptans and 20 disulfides, belonging to the aliphatic, aromatic and heterocyclic series of compounds, was studied. The molecular weights of the polymers obtained at low levels of polymerization were determined, and quantitative data on the rate of disappearance of highly active mercaptans during the polymerization was also obtained.

2. The magnitudes of the chain transfer constants calculated from these data showed that not only mercaptans, but disulfides as well, can transfer chains, and that the degree of activity of either kind of compound is influenced by the structure of the radicals bound to the sulfur.

TABLE 4

Type of regulator	R-S-H				R-S-S-R			
R	$\frac{[RSH]}{[M]}$	% of polymer	[η]	$\frac{1}{p}\cdot 10^3$	$\frac{[R_2S_2]}{[M]}\cdot 10^3$	% of polymer	[η]	$\frac{1}{p}\cdot 10^3$
C_6H_5-	2.08	7.1	1.354	0,370	2.08	3.6	1,062	0.52
	4.16	8.8	1.070	0.514	4.16	3.6	0.760	0.83
	8.33	12.1	0.748	0.849	8.33	3.8	1.536	1.35
$p-CH_3C_6H_4-$	0.00	3.4	2.074	0.200	2.08	4.1	1.062	0.52
	4.16	13.8	1.125	0.479	8.33	4.1	0.494	1.14
	8.33	15.6	0.770	0.815	12.5	5.0	0.388	2.13
$p-C_2H_5OC_6H_4-$	2.08	10.6	1.144	0.47	1.04	3.6	1.010	0.56
	4.16	13.0	0.820	0.74	2.08	3.6	0.723	0.89
	—	—	—	—	4.16	3.8	0.479	1.58
$\alpha-C_{10}H_7-$	2.08	8.7	1.112	0.49	0.52	3.8	0.646	1.04
	4.16	13.0	0.867	0.69	1.04	4.0	0.432	1.83
	8.33	16.1	0.700	0.93	2.08	4.7	0.273	3.48
$\beta-C_{10}H_7-$	2.08	10.4	0.946	0.61	0.416	3.6	1.340	0.375
	4.16	9.7	0.710	0.91	1.04	3.8	0.992	0.572
	—	—	—	—	4.16	4.3	0.475	0.603
	1.04	3.5	1.070	0.51	0.26	3.3	0.714	0.91
	2.08	3.5	0.829	0.74	0.52	3.8	0.470	1.63
	4.16	4.1	0.578	1.22	1.04	3.6	0.300	3.05
	0.104	4.3	1.941	0.223	0.52 *	3.8	0.220	4.71
	0.208	4.3	1.820	0.244	1.04	4.0	0.142	8.69
	—	—	—	—	2.08	5.2	0.095	15.26
C_6H_5CO-	0.104	3.8	0.720	0.89	1.04	3.8	1.514	0.32
	0.208	3.1	0.508	1.46	4.16	4.3	1.242	0.42
	0.416	3.8	0.261	2.35	8.33	4.0	0.614	1.12
$HOCOCH_2-$	0.104	3.6	0.430	1.84	0.42	3.6	1.564	0.30
	0.208	3.6	0.281	3.34	1.25	3.3	1.140	0.47
	0.416	3.6	0.190	5.78	2.08	3.5	0.950	0.61
$o-HOCOC_6H_4-$	0.104	3.6	0.434	1.82	0.104 **	3.6	0.462	1.67
	0.208	3.5	0.280	3.36	0.208	3.5	0.270	3.53
	0.416	3.5	0.183	6.09	0.416	3.6	0.184	6.05

* R = $(CH_3)_2CHOCS-$

** The regulator was CH_3COSH

3. The introduction of aromatic radicals into the alpha-position to the SH group markedly increases the activity of the alkylmercaptans, but the direct linkage of this group with aromatic nuclei or heterocyclic rings leads to a marked reduction in the activity of the mercaptan.

4. A considerable increase in the constants is also observed upon the introduction of alkoxy or carboxylic groups into the alpha-position to the SH group in aliphatic mercaptans, and into the ortho-position to the SH group in thiophenols, which can be explained by the formation of intramolecular hydrogen bonds of the S-H ... O type with the formation of 5- and 6-membered rings.

5. Dialkyldisulfides are distinguished by a low activity. Replacement of the alkyl groups by aromatic and heterocyclic radicals causes, however, a marked increase in the values of the chain transfer constants, as a consequence of which many aromatic disulfides display a greater activity than the corresponding thiophenols. Of the disulfides investigated, diisopropyldixanthogendisulfide proved to be exceptionally active.

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SYNTHESIS AND CONVERSION OF α - GLYCOLS OF THE ETHYLENIC SERIES. II

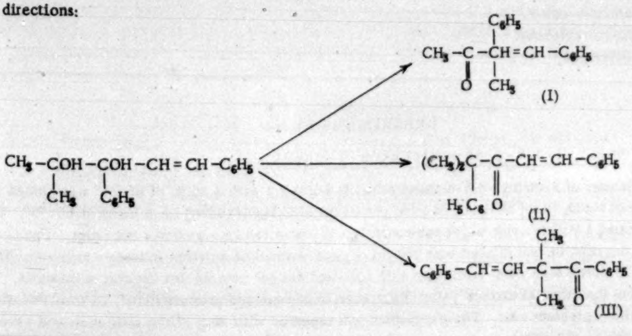
L. F. Chelpanova and V. A. Kormer

The investigation of the conversions of α-glycols (pinacols) of the ethylenic series under the influence of acidic catalysts is of interest not only as an attempt to fill the specific gap in the literature concerning the ethylenic α-glycols, but also as an opportunity to observe the manifold forms of conversions which are observed among the pinacols of the acetylenic series [1].

In the present work are described the conversions of the trans isomer of 2-methyl-2,5-diphenylpentene-4-diol-2,3 heated in the presence of 14 and 20% alcoholic solutions of sulfuric acid. This glycol was obtained by the catalytic hydrogenation of the corresponding acetylenic glycol – 2-methyl-3,5-diphenylpentyn-4-diol-2,3 [2].

On heating the trans isomer of the ethylenic glycol (m.p. 85-86°) with a 14% alcoholic solution of H_2SO_4 to 55-60°, about 70% of the initial glycol (m.p. 85-86°) was recovered, as well as about 5% of a yellow-orange oily substance which was not investigated on account of the small yield; consequently, subsequent experiments were carried out with a 20% alcoholic solution of H_2SO_4 at 60-70°. Under these conditions 30% (calculating on the basis of the initial glycol) of a light yellow oily substance with a b.p. of 210° at 15 mm was isolated from the acidic solution. The substance had an empirical formula of $C_{18}H_{18}O$, gave a negative reaction for the hydroxyl group, and decolorized an aqueous solution of potassium permanganate and bromine water. Two isomeric dinitrophenylhydrazones with melting points of 68° and 172° were isolated as a result of the action on it of 2,4-dinitrophenylhydrazine (similar cases have been described in the literature [3]).

The formation of an unsaturated ketone is satisfactorily explained by the assumption that the glycol under investigation undergoes the pinacolic rearrangement in the presence of H_2SO_4 which is observed in ditertiary α-glycols under the influence of acidic catalysts. In the present case, the reaction can theoretically go in three directions:



$$CH_3-COH(CH_3)-COH(C_6H_5)-CH=CH-C_6H_5 \rightarrow CH_3-C(=O)-C(C_6H_5)(CH_3)-CH=CH-C_6H_5 \quad (I)$$

$$CH_3-COH(CH_3)-COH(C_6H_5)-CH=CH-C_6H_5 \rightarrow (CH_3)_2C(C_6H_5)-C(=O)-CH=CH-C_6H_5 \quad (II)$$

$$CH_3-COH(CH_3)-COH(C_6H_5)-CH=CH-C_6H_5 \rightarrow C_6H_5-CH=CH-C(CH_3)_2-C(=O)-C_6H_5 \quad (III)$$

The structure of the unsaturated ketone was demonstrated by oxidation with an aqueous solution of potassium permanganate while the solution was heated. The oxidation products – acetophenone, acetic and benzoic acids – permit the structure of 3-methyl-3,5-diphenylpenten-4-one-2 (I) to be assigned to this substance. The oxidation data were confirmed by investigation of the absorption spectrum of the ketone in the infrared and ultraviolet regions.

In view of the theoretical possibility of obtaining three different unsaturated ketones, we compared the ultraviolet absorption curves of the following substances: the trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3, the trans isomer of 3-methyl-3,5-diphenylpenten-4-one-2, benzalacetone, syn .-methyl-phenylethylene and propylphenylketone.* It is evident from the figure that the absorption curves of the ketone being investigated are characterized by the presence of two bands with λ 2990 amd 2500 A. The curves of the initial glycol and the ketone being investigated have an identical kind of absorption with a maximum λ 2500 A. We assumed that the absorption band with λ 2500 A was caused by the presence in the initial glycol of the atomic grouping $-CH=CH-C_6H_5$, which is preserved in the transformation product. This is quite well confirmed by the absorption curve of $CH_3-CH=CH-C_6H_5$ which has one band with λ 2540 A. The preservation of the absorption band with λ 2500 A is caused by the presence of the atomic grouping $-CH=CH-C_6H_5$, which is possible in the ketone under investigation only when the latter is isolated from the carbonyl group. In the opposite case, as is evident from the absorption curve of benzalacetone, the band with λ 2500 A does not appear.

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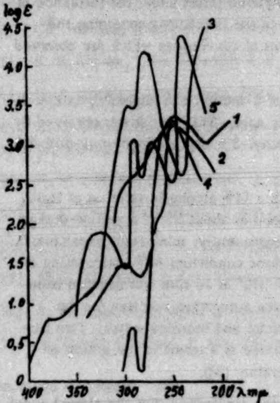
* The ultraviolet absorption spectra were recorded on a ISP-22 quartz spectrograph. An "Etalon" works hydrogen lamp served as the source of ultraviolet radiation with a continuous spectrum. A cuvette with a variable thickness and with a maximum layer thickness of 10 mm was used in taking the spectra. Hexane solutions of concentrations varying from 0.01 to 0.001 mole/ml were investigated. The method of equal blackening was used for the photomeasurements.



1) Trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3; 2) trans isomer of 3-methyl-3,5-diphenylpenten-4-one-2; 3) benzalacetone; 4) sym.-methylphenyl ethylene; 5) propylphenylketone.

The absorption band in the ketone under investigation with λ 2990 A characterizes the presence of the carbonyl group. The curve cited for the absorption of

$$C_6H_5-CO-CH_2-CH_2-CH_3$$

excludes the presence in the ketone under investigation of the atomic grouping (C_6H_5-CO-).

What has been set forth above completely confirms the data obtained during the oxidation, and permits the structure of 3-methyl-3,5-diphenylpenten-4-one-2 (I) to be assigned to the isomerization product; this is confirmed quite well by the available literature data, which refer to the great mobility of a hydroxyl group which stands in the alpha-position to an unsaturated bond [4].

EXPERIMENTAL

Preparation of 3-methyl-3,5-diphenylpenten-4-one-2 (I)

4 g of the trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3 with a m.p. of 85-86° was heated with a 20% alcoholic solution of H_2SO_4 [5 ml of H_2SO_4 (d 1.84) per 40 ml of C_2H_5OH (96%)] for 5 hours at 60-70°. The mixture gradually assumed a yellow color which subsequently was converted into a cherry red color. Upon completion of the heating the mixture was diluted with 250 ml of cold water, and an ether extract was made. The acidic solution was neutralized after ether extraction with soda and did not contain any organic substances. This substance, obtained from the ethereal extract [after distillation under reduced pressure (210°, 15 mm)] consisted of a light yellow oil with a pleasant odor. The experiment was repeated with 30 g of the substance and gave analogous results:

d_4^{20} 1.0506; n_D^{20} 1.5782; MR_D 79.00; Calc. 77.70
9.08 mg. sub.: 28.80 mg CO_2; 5.99 mg H_2O. 7.27 mg sub.: 23.04 mg CO_2; 4.77 mg H_2O. 0.2333 g sub.; 17.7 g benzene: Δt 0.26°. Found %: C 86.56, 86.49; H 7.38, 7.36; M 253.5. $C_{18}H_{18}O$. Calculated %: C 86.40; H 7.20; M 250.

The substance reacted with bromine water and with an aqueous solution of potassium permanganate, showed the absence of the hydroxyl group with Grignard reagent and the presence of the keto group with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazones of the substance under investigation were obtained under the usual conditions [5]. In 5 minutes after mixing alcoholic solutions of the substance and 2,4-dinitrophenylhydrazine, a red precipitate settled out, which was filtered off and recrystallized from ethyl alcohol with a small addition of ethyl acetate.

On the following day after recrystallization, red crystals settled out. The mother liquor was left to stand. Toward the end of the day, light yellow crystals precipitated from it which were once more recrystallized from alcohol. The red crystals melted at 68-70°, the yellow, at 172-173°.

Investigation of the Dinitrophenylhydrazone with a M.P. of 68-70°.

4.01 mg sub.: 0.453 ml N_2 (22°, 765 mm). 3.38 mg sub.: 0.370 ml N_2 (19°, 775 mm). 7.02 mg sub.: 17.23 mg CO_2; 3.21 mg H_2O. Found %: N 13.16, 13.06; C 66.90; H 5.18. $C_{24}H_{22}O_4N_4$. Calculated %: N 13.02, C 67.00; H 5.11.

Investigation of the Dinitrophenylhydrazone with a M. P. of 172-173°.

5.74 mg sub.: 0.655 ml N_2 (20°, 760 mm). 4.77 mg sub.: 0.496 ml N_2 (20°, 761 mm). Found %: N 12.89, 12.95. $C_{24}H_{22}O_4N_4$. Calculated %: N 13.02.

The two hydrazones with different melting points were, apparently geometrical isomers. Upon heating the red isomer (m.p. 68-70°) above its melting point it was converted into the yellow isomer with a m.p. of 172-173°. Both hydrazones gave a negative pyrazoline reaction.

Oxidation of the ketone

An acetophenone, which gave a 2,4-dinitrophenylhydrazone with a m.p. of 237°, was isolated by oxidation with an aqueous solution of potassium permanganate (1.5 g ketone; 0.9 g $KMnO_4$; 60-70°) and by the usual separation of the neutral and acidic oxidation products from the neutral substances. The aqueous solution of the acidic products contained benzoic acid with a m.p. of 122.0°, which was characterized by a mixed melting point test, and acetic acid, characterized by analysis of the silver salt.

0.0535 g sub: 0.0582 g CO_2; 0.0156 g H_2O. Found %: C 14.57; H 1.61; Ag 65.01. CH_3COOAg Calculated %: C 14.45; H 1.81; Ag 64.67.

SUMMARY

Upon the dehydration of 2-methyl-3,5-diphenylpentene-4-diol-2,3 under the influence of a 20% alcoholic solution of H_2SO_4, a pinacolic rearrangement occurs, as a result of which 3-methyl-3,5-diphenylpenten-4-one-2, which has not been described in the literature, is formed. Two 2,4-dinitrophenylhydrazones of this ketone with m.p. of 68-70 and 172-173° were obtained.

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CONFIGURATION AND PROPERTIES OF UNSATURATED ACIDS AND THEIR DERIVATIVES

II. PROPERTIES OF CINNAMIC ACIDS AND THEIR ESTERS

A. K. Plisov and A. I. Bykovets

We have shown in preceding communications [1] that the influence of radicals at the double bond is manifested differently in the cis and trans forms of such unsaturated acids as oleic and petroselinic acids and their esters. In addition, it was established that the cis and trans forms of the esters of these acids act differently in reactions, associated with their ester group; at the same time, the magnitude and structure of the alcohol radical had a definite influence.

These facts impelled us to set up experiments to elucidate and compare the reactivity of the cinnamic acids and their esters. It was necessary to elucidate the influence on the reactivity of these compounds of a phenyl and carboxyl or ester group, directly linked to the carbon atoms which were joined to the double bond.

The results of the experiments set up for this purpose are in excellent agreement with the data of our earlier experiments on other materials. In this case, too, it can be said that the cis and trans forms of the cinnamic acids (or their derivatives) are identically reactive both in relation to reactions at the double bond, and in relation to reactions associated with the ester group. In other words, the cinnamic acids and their esters manifest chemical activity in accordance with the theory of steric hindrance. Actually, trans-cinnamic acid with a m.p. of 133° is oxidized and hydrogenated considerably more slowly than the cis acid.

It is necessary to assume that the phenyl group, which is located on one side of the double bond, and the carbonyl and ester groups which are located on the other, hamper the access of the reagent to the double bond. In the cis form, in which both groups are found on only one side of the double bond, this influence is exerted to a lesser extent.

As regards saponification of the propyl esters of the cinnamic acids, the opposite picture is observed here, as one was bound to expect. The propyl ester of trans-cinnamic acid is saponified more quickly than the ester of cis-cinnamic acid.

Thus, in the present case, the ester group manifests its chemical activity differently in the cis and trans forms of the esters of the cinnamic acids.

It was necessary to obtain the difficultly-accessible cis-cinnamic acid for the study of these questions. The best way of preparing it was by isomerizing trans-cinnamic acid under the influence of ultraviolet light; under these conditions, as is well known, various forms of cis-cinnamic acid are obtained; most frequently we obtained one with a m.p. of 42° and another with a m.p. of 58°.

Up to the present time the opinion has been held that the three well-known forms of cinnamic acid with m.p. of 42, 58, and 68° are different crystalline modifications of the same acid, the molecules of which can be grouped in three ways in the crystals. However, if the results of our experiments involving the hydrogenation and oxidation of the cinnamic acids with m.p. of 42 and 58° are taken into account, it is impossible to agree with this. We firmly established that the two mentioned forms of cis-cinnamic acid are hydrogenated and oxidized in suitable solvents at an identical rate. Consequently, the question is not of the influence of crystalline forms on the reactivity, but of the different spatial configuration of the two forms of this acid. There is no sufficiently clear-cut information regarding this in the literature. It is possible that, in the present case, we have to do with a very rare phenomenon, associated with the limiting of the free rotation of the phenyl group in cis-cinnamic acid. The latter may be caused by the formation of hydrogen bonds between the phenyl and carbonyl groups. If we admit the possibility of three-dimensional, but not of plane distribution of the six carbon atoms of the benzene nucleus, then, probably, this can be explained by the presence of four forms of cis-cinnamic acid (allocinnamic acid). The three cis-cinnamic acids mentioned above are usually cited in the literature, but in fact, an additional, fourth acid with a m.p. of 36°, described by Erlenmeyer-Jr. [2] is also known. This form of cis-cinnamic acid has not been sufficiently studied, and is not usually mentioned in the current literature.

EXPERIMENTAL

Preparation of the Cinnamic Acids and their Propyl Esters

Commercial trans-cinnamic acid with a m.p. of 133° was used in the work. Cis-cinnamic acid was prepared by us, starting from the trans-cinnamic acid, via irradiation with ultraviolet light for 100 hours, of its benzene solution, placed in a quartz flask. After separating the mixture of acids obtained with the aid of the aniline salts and appropriate purification, in some cases predominantly cis-cinnamic acid with a m.p. of 42°, and in other cases, the isomer which melted at 58°, was obtained. The conditions for obtaining these isomers have been described in greater detail in the article by Stoermer [3].

The propyl ester of trans-cinnamic acid was prepared by the usual esterification reaction via heating trans-cinnamic acid with propyl alcohol in the presence of concentrated sulfuric acid. After purification, the ester had a b.p. of 283° and n_D^{25} 1.409.

The propyl ester of cis-cinnamic acid, still not described in the literature, was prepared from the silver salt of cis-cinnamic acid with a m.p. of 58° and propyl bromide. The propyl ester of cis-cinnamic acid was a colorless liquid with a pleasant, flower-like odor and a m.p. of 122-124° (at 15 mm); n_D^{20} 1.4244. The ester was quite soluble in alcohol, acetic acid and benzene.

Hydrogenation of the Cinnamic Acids

Equal samples of the cinnamic acids were placed in identical hydrogenation vessels ("goose vessels") for the hydrogenation. To weighed samples of about 0.5 g, the calculated quantity of soda solution was added and palladium catalyst, precipitated on $BaSO_4$ (0.05 g of the catalyst contained 0.001 g of Pd) was introduced. The vessels with the samples were placed in a shaking apparatus, and purified hydrogen was simultaneously passed in at low pressure in an appropriate manner.

The results of the hydrogenation of the cinnamic acids are presented on Fig. 1. There is a notable difference between the quantities of hydrogen added not only to the cis and to the trans forms, but even to the cis-cinnamic acids with differing melting points.

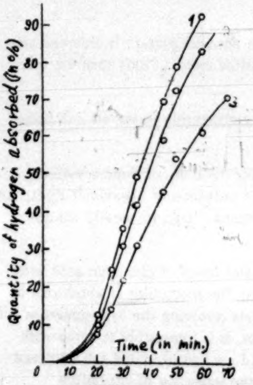

Fig. 1. Hydrogenation of the cinnamic acids.
1) Cis-cinnamic acid with a m. p. of 58°; 2) cis-cinnamic acid with a m.p. of 42°; 3) trans-cinnamic acid with a m.p. of 133°.

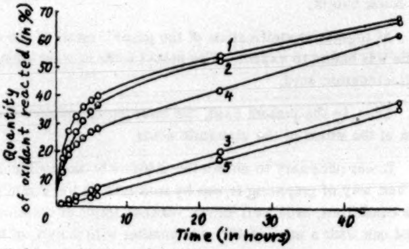

Fig. 2. Oxidation of the cinnamic acids.
1) and 4) Cis-cinnamic acid with a m.p. of 58°; 2) cis-cinnamic acid with a m.p. of 42°; 3) and 5) trans-cinnamic acid.
1), 2) and 3) at a temperature of 23°; 4) and 5) at a temperature of 15°.

Oxidation of the Cinnamic Acids and their Esters

Various oxidizing agents were tested in the study of the oxidation of cinnamic acids: $KMnO_4$ in acetone and aqueous solutions, $K_2Cr_2O_7$ in acetic acid solution, hydrogen peroxide, benzoyl peroxide and perbenzoic acid. Some of them ($KMnO_4$ and H_2O_2) proved unsuitable as a consequence of the fact that the oxidation with these oxidants proceeded with great speed, while others—benzoyl peroxide and perbenzoic acid—did not react at all. The result of these experiments was that $K_2Cr_2O_7$, dissolved in glacial acetic acid, proved usable for observations on the rate of oxidation.

Equimolecular quantities of 0.1 N $K_2Cr_2O_7$ solution in glacial acetic acid were added in our experiments to two identical samples of the acids or their esters, dissolved in acetic acid. Each of the forms of cinnamic acid was converted into benzaldehyde as a result of the oxidation.

Curves which characterize the relative rates of oxidation of cinnamic acids and their propyl esters at temperatures of 15° and 23° are presented in Figs. 2 and 3. The great difference between the relative rates of oxidation of the cis and trans acids and of their esters is also noticeable here. The esters are oxidized considerably more slowly than the corresponding acids. It is very important to note that oxidation of cinnamic acids with m.p. 42 and 58° proceeds at rates which are not identical; the acid with m.p. 42° is oxidized somewhat more slowly than its isomer with a m.p. of 58°.

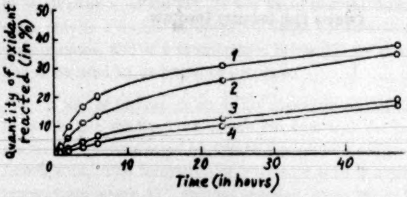

Fig. 3. Oxidation of the propyl esters of the cinnamic acids.
1) and 2) The propyl ester of cis-cinnamic acid;
3) and 4) the propyl ester of trans-cinnamic acid.
1) and 3) at a temperature of 23°; 2) and 4) at a temperature of 15°.

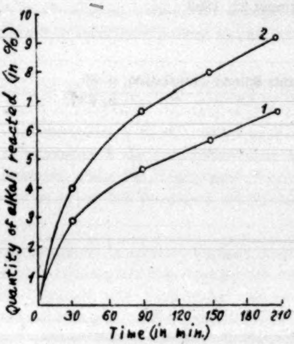

Fig. 4. Saponification of the propyl esters of the cinnamic acids. 1) The propyl esters of cis-cinnamic acid; 2) the propyl esters of trans-cinnamic acid.

Saponification of the Propyl Esters of the Cinnamic Acids

Identical samples of the esters, dissolved in anhydrous alcohol, were subjected to saponification with alcoholic alkali under identical conditions. The saponification was carried out with a 0.1 N solution of alkali at 20°. The alkali was taken in an equimolecular quantity in relation to the amount of the ester sample. 5 ml samples of the reaction mixture were taken at regular intervals from the small flasks, which were placed in a thermostat. The quantity of unreacted alkali in each sample was determined.

The change in the quantity of alkali with time during the saponification of the propyl esters of the cinnamic acids is shown in Fig. 4. The ester of trans-cinnamic acid is saponified more rapidly than the ester of the cis acid.

SUMMARY

1. The propyl ester of cis-cinnamic acid was synthesized and its properties were described.

2. A difference in the relative rates of hydrogenation of the cis-and trans-cinnamic acids was established: cis-cinnamic acid adds hydrogen more readily.

3. The oxidation of the cinnamic acids and their esters proceeds at varying rates. Cis-cinnamic acid and its ester are oxidized more quickly than trans-cinnamic acid and its ester; the esters are oxidized more slowly than the corresponding acids.

4. The saponification of the propyl ester of cis-cinnamic acid proceeds more slowly than saponification of this ester of trans-cinnamic acid.

5. It was established that the so-called "crystalline modifications" of cis-cinnamic acid (allocinnamic acid) with a m.p. of 42 and 58° have varying reactivities: cis-cinnamic acid with a m.p. of 42° is hydrogenated and oxidized more slowly than its isomer with a m.p. of 58°.

6. A hypothesis concerning the configuration of the cis form of the cinnamic acids was proposed.

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* See Consultants Bureau Translation, p. 69.
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CONVERSION AND SYNTHESIS OF CARBOHYDRATES

XI. INVESTIGATION IN THE FIELD OF KETOSE OXIDATION

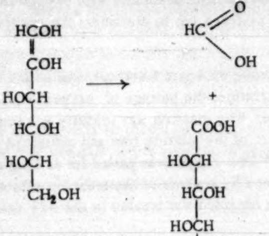
V. M. Berezovsky and L. I. Strelchunas

In one of the preceding communications [1], one of us studied the cleavage oxidation of aldose by oxygen in an alkaline medium [2]. It was found that the formation of d-arabonic acid by the oxidation of d-glucose proceeds only in a narrow temperature range between 40 and 50°; at a temperature above 50°, another reaction-route predominates, and at a temperature below 40° the rate of the reaction becomes too small for the oxidation reaction to be used for preparative purposes.

It was of interest to study the cleavage oxidation of ketose, in particular, the oxidation of 1-sorbose by oxygen in an alkaline medium [3], which proceeds with the formation of 1-xylonic acid. We showed that the oxidation reaction is accompanied by the absorption of 2 oxygen atoms and the splitting off of 1 carbon atom in the form of formic acid. The formation of 1-xylonic acid in a yield of 37% proceeds in the temperature range 24-42°; at a temperature above 42°, another reaction-route begins to predominate, while the oxygen requirement of 2 atoms of oxygen per molecule of ketose is the same, and at a temperature below 24°, the rate of the reaction becomes insignificant.

The circumstance that, in the oxidation of ketohexose by oxygen in an alkaline medium, 2 atoms of oxygen are absorbed, furnishes a basis for assuming that the formation of 1-xylonic acid from sorbose can not proceed via the intermediate formation and subsequent oxidation of 2-keto-1-gulonic acid, since in this case no less than 3 oxygen atoms would be required (in accord with the data on the oxidation of 2-keto-1-gulonic acid by hydrogen peroxide with 2 atoms of oxygen [4]). The absence of 2-keto-1-gulonic acid in the reaction described by us was established by a negative test for the formation of ascorbic acid.

The cleavage of 1 carbon atom with the formation of formic acid and the formation of pentonic acids in the oxidation of ketohexose by oxygen in an alkaline medium gives a basis for assuming that the mechanism of this reaction is of the same kind as the mechanism of the oxidation of aldohexose under the same conditions. The probable mechanism of the reaction of cleavage oxidation of sorbose by oxygen in an alkaline medium consists in an initial tautomeric conversion of the noncyclic form of 1-sorbose into the endiol form with an unsaturated bond between the first and second carbon atoms, which then undergoes oxidation by molecular oxygen with rupture of ethylenic bond and formation of formic and 1-xylonic acids:



Side reactions can proceed due to enolization at the second and third carbon atoms and, further, with migration of the double bond, at the third and fourth carbon atoms and so forth; in this case the oxidation reaction will be accompanied by the formation of glycolic and tetronic acids and other oxidation products.

1-Xylonic acid was isolated from the oxidized solution in the form of the double cadmium salt with cadmium bromide; if the volatile organic acids and excess quantity of mineral salts are not preliminarily eliminated from the solution, then the isolation of the double salt of cadmium xylonate from the solution is made difficult.

The rate constant of the reaction of sorbose oxidation at 40° is K = 0.05446 as against K = 0.01161 for the glucose oxidation reaction at the same temperature. Thus, a considerably higher reactivity can be established for ketose in comparison with aldoses (approximately 4.7 times greater) as regards the oxidation with oxygen in an alkaline medium. The increased reactivity of ketose is in complete accord with well known facts, for example, the predominant condensation of the keto groups of reductone (the enol of hydroxymalonic aldehyde) with the maximally reactive amino group in position 5 in 2,4,5-triamino-6-hydroxypyrimidine [5].

The formation of a small quantity of oxalic acid (about 0.8% of the theoretical) is observed in the cleavage oxidation of 1-sorbose by oxygen in alkaline medium, along with the formation of 1-xylonic acid. A similar type of side reaction was previously observed for the oxidation of aldose [1].

The method of single-stage preparation of 1-xylonic acid by cleavage oxidation of 1-sorbose presents considerable advantages in comparison with the two-stage method of oxidizing 1-sorbose, which proceeds in a sodium bicarbonate solution by the action of atmospheric oxygen in the presence of palladium catalyst, initially with formation of 2-keto-1-gulonic acid, and then with its subsequent oxidation by hydrogen peroxide.

EXPERIMENTAL

Cadmium 1-xylonate·cadmium bromide.

73 g of 1-sorbose, 60 g of potassium hydroxide in a solution (or an equivalent quantity of sodium hydroxide) and water to a volume of 560 ml were introduced into a rotating autoclave, filled with metallic gauze. The sorbose was oxidized with oxygen at 30-35° for 3 hours at an initial pressure of 30-35 atm.; 1 mole of oxygen was absorbed per mole of ketose. Upon completion of the oxidation, less than 0.5% of unchanged sorbose remained.

The oxidized solution was neutralized with hydrochloric acid (d 1.19, 70-80 ml) to a violet coloration with congo red and was concentrated in a vacuum. Water was added to the partially crystallized syrupy residue and it was again concentrated in a vacuum; this process was repeated 3-4 times, until the almost complete elimination of the volatile organic acids. The mineral salts were then filtered off, washed with ice water and 1-xylonic acid was isolated from the filtrate in the form of difficultly soluble double cadmium salt with cadmium bromide. For this purpose, 150 ml of water and, gradually, while heating to boiling, 35 g of cadmium carbonate, were added to the filtrate; upon completion of the evolution of carbon dioxide, the solution was filtered and 55 g of cadmium bromide was added to it. After crystallization 32.4 g (22%) of the double salt of cadmium xylonate was obtained in the course of several days.

The substance was recrystallized from a 15-fold quantity of water for analysis.

Found %: Cd 29.70. $C_{10}H_{18}O_{12}Br_2Cd_2 \cdot 2H_2O$. Calculated %: Cd 29.95.

Kinetics of the oxidation of 1-sorbose.

The study of the cleavage oxidation reaction of sorbose with oxygen in an alkaline medium was carried out in a glass column with sealed-in porous plates, 4 cm in diameter; the apparatus used has been described previously [1].

230 ml of aqueous solution, containing 36.5 g of 1-sorbose, was added to the column, and at a temperature several degrees below the assigned temperature, the passage of oxygen was initiated, after which 50 ml of a 40% solution of sodium hydroxide was added. The reaction was initially accompanied by the evolution of heat. After the solutions were mixed, the temperature of the mixture rose and remained constant throughout the entire duration of the experiment to within ±0.2°. The oxygen was passed for as long as was necessary for the oxidation of no less than 95% of the sorbose (determined by analysis of the reducing substance). Upon completion of the oxidation reaction, the colorless solution obtained was treated in the way described above with the object of isolating the xylonic acid from it.

Since the reaction proceeds chiefly in a fine film (and to a lesser extent due to solution of the gas in the liquid), the oxygen was passed at a rate of 1.2 liter/minute (0.32-0.38 liter/minute per cm² of the surface of the Schott No. 3 plate), which corresponded to its optimal dispersion in the liquid and to the creation of a maximum contact surface of the liquid and gaseous phases. By diminishing the rate of passage of oxygen to 0.5 liter/minute, the surface of the film was diminished, which was accompanied by a diminution in the rate of the reaction.

The temperature factor has great influence not only on the rate of the oxidation of sorbose by oxygen in an alkaline medium, but also on the direction of the reaction. The results of experiments at variable temperature, conducted under conditions which created a maximum surface film with other conditions constant, are depicted in Fig. 1.

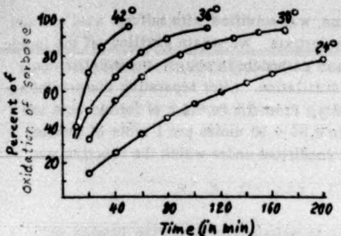


Fig. 1. Influence of temperature on the rate of the oxidation of sorbose by oxygen in an alkaline solution.

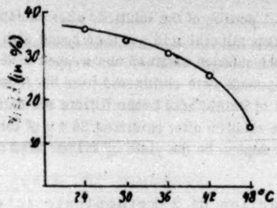


Fig. 2. Dependence of the yield of the complex salt of cadmium xylonate on the temperature.

At 24°, 25% of the sorbose undergoes oxidation in the first 40 minutes, while more than 6 hours is required for the oxidation of 95%. At 30°, 54% of the sorbose is oxidized in the first 40 minutes and 3 hours are necessary for 95% oxidation; at 36°, 68% of the sorbose is oxidized in the first 40 minutes and 95% in 1 hour and 45 minutes; at 42°, 95% of the sorbose is oxidized in the first 49 minutes.

Upon raising the reaction temperature above 36°, the yield of xylonic acid is markedly diminished with the simultaneous complete oxidation of the initial sorbose; the optimal temperature lies in the 24-36° range. The yields of xylonic acid depending on the oxidation reaction temperature (the yield is lowered from 36.4% to 13.6% when the temperature is raised from 24° to 48°) are presented in Fig. 2.

The rate constant of the cleavage oxidation of sorbose with oxygen was determined by us in an apparatus with a Schott No. 3 filter, 4 cm in diameter, with an optimal quantity of oxygen being passed (1.2 liter/minute); the temperature variation was within limits of ± 0.1°.

The rate constants of the reaction, which was determined by us to be monomolecular, were

$$K_{(24^\circ)\ \mathrm{av.}} = 0.00747\ ; \quad K_{(30^\circ)\ \mathrm{av.}} = 0.01840;$$

$$K_{(40^\circ)\ \mathrm{av.}} = 0.05401.$$

The deviations of the values of the rate constants of the reaction from the average amounted to from 2 to 3.2%. The satisfactory constancy of $K_{\mathrm{av.}}$ showed the monomolecular character of the cleavage oxidation of sorbose by oxygen in alkaline medium. The reaction is complex as regards the variety of products obtainable; however, the reaction of monoses with oxygen proceeds in strictly equimolecular ratios. Of the two reacting molecules – sorbose and oxygen – the variable quantity is the sorbose concentration; the quantity of oxygen is stable and excess.

Just as in the oxidation of glucose [1], there is an induction period for the oxidation reaction of sorbose of up to 15 minutes, in which period the rate constant of the reaction differs from its average value.

The temperature coefficient of the rate of the reaction amounts for temperatures of 30 and 40° to:

$$\frac{K_{(40^\circ)}}{K_{(30^\circ)}} = 2.93.$$

The activation energy, calculated by the Arrhenius equation on the basis of the rate constants of the reaction for 30 and 40°, amounts to A = 20300 calories.

Determination of oxalic acid

After the oxidation of 36.5 g of sorbose, we found from 0.462 to 0.463 g of oxalic acid in the solution. The quantity of oxalic acid is independent of the temperature conditions under which the reaction is conducted and of other variable factors. The determination was carried out by isolating oxalic acid from the neutralized solution in the form of its calcium salt with subsequent titration with potassium permanganate [1].

Determination of formic acid

An 0.1 portion of the solution,* after oxidation of 36.5 g of sorbose, was acidified with sulfuric acid solution and the excess mineral acid was then bound with potassium ammonium tartrate. We steam distilled off the formic acid from the solution obtained and trapped it with a solution of calcium carbonate in water; the volatile non-acidic compounds were eliminated from the receiving flask by steam distillation. After separating the precipitate, the content of formic acid in the filtrate was determined oxidimetrically. From 7.8 to 8.4 g of formic acid was found in the solution after oxidizing 36.4 g of sorbose; this amounted to 0.84-0.90 moles per 1 mole of sorbose, and did not depend on the yield of xylonic acid or on the temperature conditions under which the reaction was conducted.

Determination of 2-ketogulonic acid

10 ml of the solution after the oxidation of the sorbose was neutralized with hydrochloric acid (about 1 ml), 10 ml of hydrochloric acid (d 1.19) was added to the mixture and was heated with a reflux condenser for 90 minutes. Titration with potassium iodate demonstrated the absence of ascorbic acid and, consequently, the absence of 2-ketogulonic acid in the solution under investigation.

A control experiment with the addition to the solution under investigation of 0.160 g of known 2-ketogulonic acid and with the analysis conducted in the manner indicated above, demonstrated the presence of 0.107 g of ascorbic acid (i.e., 0.53% in the solution), which indicates that the precision of the method used was sufficiently great.

SUMMARY

1. The kinetics of the cleavage oxidation of l-sorbose by oxygen in alkaline medium was studied. In alkaline medium, ketoses react with oxygen in a strictly equimolecular ratio.

2. It was shown that ketoses have a considerably greater reactivity (approximately 4.7 times greater) than aldoses, as regards oxidation by oxygen.

3. It was shown that the oxidation of sorbose with the formation of xylonic acid proceeds in a narrow temperature range—at a temperature above 42°, another reaction route predominates.

4. The formation of oxalic acid as one of the side products of the reaction was established.

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RECIPROCAL REACTION OF TRIALKYLSILANES WITH MONOCARBOXYLIC ACIDS.

A NEW METHOD OF SYNTHESIZING TRIALKYLACYLOXYSILANES AND THEIR PHYSICAL PROPERTIES

B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov

The present work is a continuation of our investigations devoted to the study of the reaction of the Si–H bond in silicoorganic compounds. We have previously studied [1] the reaction of trialkylsilanes with alcohols which is catalyzed by alcoholates of the alkali metals and which leads to the formation of trialkylalkoxysilanes in a yield of 80 - 90% of the theoretical:

$$R'OH + HSiR_3 \xrightarrow{OR^-} R'OSiR_3 + H_2.$$

The possibility of replacing the hydrogen atom bound to the silicon atom with a primary, secondary or tertiary alkoxy group was demonstrated as a result of the investigation.

Working out a method of replacing the hydrogen atom attached to the silicon atom with an acyloxy group by an analogous scheme was an additional goal of our work:

$$R'COOH + HSiR_3 \longrightarrow R'COOSiR_3 + H_2.$$

There are certain indications in the literature regarding the possibility of such substitution [2-4]. Reilly and Post [2], for example, observed the conversion of the Si–H bond into the Si–$OCOCH_3$ bond in the reaction of trialkoxysilanes with acetic anhydride:

$$(RO)_3SiH + 2(CH_3CO)_2O \longrightarrow (RO)_2Si(OCOCH_3)_2 + CH_3CHO + CH_3COOR.$$

Kautsky and Hirsch [3] indicate that acyloxy derivatives of siloxene are formed as a result of its reaction at the Si–H bond with carboxylic acids which can be represented by the scheme:

$$\equiv SiH + R'COOH \longrightarrow \equiv SiOCOR' + H_2.$$

Acid anhydrides react analogously:

$$\equiv SiH + (RCO)_2O \longrightarrow \equiv SiOCOR' + RCHO.$$

However, no one has tried to use these reactions for the preparative formation of silicoorganic esters of carboxylic acids. Up to the present time, these compounds have been obtained by the reaction of halogensilanes by organic acids [5-10], their salts [11-16], anhydrides [5], or esters [17], and also by the action of acid anhydrides on alkoxy substituted silanes [2,16,18-22] and amino substituted silanes [16]. The yields of acyloxy derivatives as a result of the indicated methods of synthesizing them rarely exceeds 50%. Trialkylacyloxysilanes can be prepared by the reaction of trialkylsilanes with acid chlorides [23] or anhydrides [24]. The synthesis of tetraacyloxysilanes by the reaction of organic acids with SiS_2 [25] has also been described.

It has been shown, in the case of trialkylsilanes, in the present work that replacement of the hydrogen atom bound to the silicon atom by an acyloxy group can be readily accomplished by catalytic reaction with carboxylic acids or by reaction with mercury salts of organic acids, which proceeds according to the scheme:

$$R_3SiH + Hg(OCOR')_2 \longrightarrow R_3SiOCOR' + Hg + R'COOH.$$

The reaction of trialkylsilanes with organic acids is catalyzed by strong mineral acids (H_2SO_4 and HI) or by iodine. However, the best results were obtained by using a powdered mixture of aluminum and iodine, taken in a molar ratio 1:3.2 as the catalyst. The molar ratio of aluminum to the initial trialkylsilane amounted to 3.7% in all the experiments.

The reaction of trialkylsilanes with monocarboxylic acids was accomplished by heating to boiling a mixture of trialkylsilane with double the theoretical quantity of the organic acid to which the catalyst had been added. The heating was carried out until the complete cessation of evolution of the hydrogen which was always formed in the theoretical quantity. After distilling off the excess acid, the reaction mixture was distilled over metallic copper (to eliminate free iodine) and rectified in a column. The high-boiling trialkylacyloxysilanes were vacuum distilled.

The yields of trialkylacyloxysilanes amounted to 81-87% of the theoretical when they were synthesized by the indicated method.

TABLE 1

Data on the Experiments involving the Reaction of Trialkylsilanes with Monocarboxylic Acids

Starting Materials *		Maximum temperature of the mixture toward the end of the reaction.	Duration of the reaction (in hours).	Yield of $R'COOSiR_3$ (in %)
R_3SiH R =	$R'COOH$ R′=			
C_2H_5	CH_3	174*	2.5	86.4
C_2H_5	C_2H_5	190	1.0	85.1
C_2H_5	$n-C_3H_7$	207	3.0	82.0
C_2H_5	$(CH_3)_2CH$	200	1.0	83.7
C_2H_5	$n-C_4H_9$	230	2.5	83.2
C_2H_5	$(CH_3)_2CHCH_2$	220	4.0	84.0
C_2H_5	$C_2H_5(CH_3)CH$	220	2.0	83.3
C_2H_5	$(CH_3)_3C$	208	1.5	87.8
C_2H_5	$n-C_5H_{11}$	245	2.0	85.0
C_2H_5	$C_6H_5CH_2$	275	1.5	81.0
C_2H_5	C_6H_5	265	1.5	81.6
$n-C_3H_7$	$n-C_4H_9$	290	1.5	85.9
$n-C_3H_7$	$(CH_3)_2CHCH_2$	272	1.0	83.7
$n-C_3H_7$	$C_2H_5(CH_3)CH$	265	1.5	85.1
$n-C_3H_7$	$(CH_3)_3C$	255	1.5	87.1
$n-C_4H_9$	$n-C_4H_9$	295	1.5	86.9
$n-C_4H_9$	$(CH_3)_2CHCH_2$	280	1.0	85.9
$n-C_4H_9$	$C_2H_5(CH_3)CH$	269	1.5	86.6
$n-C_4H_9$	$(CH_3)_3C$	255	1.5	86.9

* The molar ratio $R_3SiH : R'COOH : AlI_3 = 1 : 2 : 0.04$;

The data presented in Table 1 (the yields of trialkylacyloxysilanes, the duration of the reaction and the maximum temperature of the reaction mixture), show that the rate of the reaction of trialkylsilanes with monocarboxylic acids is practically independent of the structure of both components. This sharply differentiates the reaction of trialkylsilanes with organic acids from their reaction with alcohols [1]. It can also be noted that in the case of aliphatic monocarboxylic acids, the increase in the dissociation constant of the acid leads to an increase in the rate of their reaction with trialkylsilanes. Trimethylacetic acid, which has the greatest dissociation constant, reacts energetically with triethylsilane even without heating.

We did not succeed in preparing triethylformoxysilane by the reaction of triethylsilane with formic acid. Although the reaction proceeded with the evolution of hydrogen, the basic reaction product proved to be hexaethyldisiloxane.

As a result of the present investigation, we synthesized 19 trialkylacyloxysilanes $R'COOSiR_3$, in which $R = C_2H_5$, $n-C_3H_7$ and $n-C_4H_9$, while R' is a primary, secondary or tertiary alkyl radical, C_6H_5 or $C_6H_5CH_2$. The physical properties of these compounds, of which 16 had been previously unknown, are presented in Table 2.

Trialkylacyloxysilanes are colorless liquids with a characteristic, pleasant odor, rather difficultly hydrolyzed by water (they are more readily hydrolyzed by alcoholic solutions of alkali which we used as the basis of their quantitative determination).

The mechanism of the reaction of trialkylsilanes with carboxylic acids which is catalyzed by a mixture of iodine and aluminum (i.e., $AlI_3 + I_2$) is presented by us in the following manner.

Trialkylsilane reacts with iodine with the formation of trialkyliodosilane:

$$R_3SiH + I_2 \longrightarrow R_3SiI + HI.$$

The thereby-formed hydrogen iodide, in the presence of AlI_3, quickly reacts with trialkylsilane, also with formation of trialkyliodosilane:

$$R_3SiH + HI \longrightarrow R_3SiI + H_2.$$

In the absence of AlI_3, the latter reaction does not proceed so smoothly, which explains the smaller yields of trialkylacyloxysilanes in the reaction of trialkylsilanes with acids in the presence of iodine alone. Trialkyliodosilane then reacts with carboxylic acid with the formation of trialkylacyloxysilane and HI, which then reacts with the trialkylsilane:

$$R_3SiI + HOCOR' \longrightarrow R_3SiOCOR' + HI,$$

$$R_3SiH\ HI \xrightarrow{AlI_3} R_3SiI + H_2 \text{ etc.}$$

The reaction of trialkyliodosilane with acid precedes its solvolytic ionization which occurs the more readily, the less the ionization constant of the acid. Due to this, the reaction proceeds as a monomolecular nucleophile substitution (S_N1 of Ingold-Hughes):

$$R_3SiI \longrightarrow R_3Si^+ + I^-.$$

$$R_3Si^+ + R'COO^- \longrightarrow R'COOSiR_3.$$

The scheme presented for the mechanism of the reaction explains the lack of dependence of the rate of the reaction of trialkylsilanes, R_3SiH, with monocarboxylic acids, RCOOH, on the structure of the R and R' radicals, since the reaction of the $RCOO^-$ ion proceeds from the apex of the R_3Si^+ tetrahedron which is formed after the removal of the I^- ion. In contrast to this, in the reaction of trialkylsilanes with alcohols, due to the difficulty of cleaving the hydride ion, the reaction proceeds as a bimolecular nucleophile substitution (S_N2); under these conditions the alkoxy group is forced to approach the silicon atom from the side of the alkyl groups, i.e., from the opposite side of the tetrahedral molecule R_3SiH,[*] which involves steric hindrance which increases with increasing size of either the alkyl radicals or of the alkoxy group.

EXPERIMENTAL

The initial trialkysilanes, their constants and analytical data have been described in one of the preceding works [27]. The monocarboxylic acids were purified by fractional distillation in a column or in a vacuum. 78% formic acid was purified by a single freezing out, after which it was vacuum distilled over phosphoric anhydride. Before distilling the acetic acid, it was purified by a two-fold freezing out. The physical constants of the acids used are presented in Table 3.

The method of analysis for silicon and the determination of the physical constants are also described in one of our works [28].

The ester number of the trialkylacyloxysilanes was determined by saponification of samples of the substances with an 0.75 N KOH solution in ethylene glycol [29].

Method of conducting the reaction

All the syntheses of trialkylacyloxysilanes were carried out in two-necked 100 ml round-bottomed flasks

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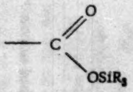
[*] The tetrahedral structure of the R_3SiH molecule has been confirmed by the data of the measurements of its dipole moments [26].

TABLE 2

Physical Properties of the 
$R'-C(=O)OSiR_3$
Trialkylacyloxysilanes, Their Analytical Data and Molecular Weight Determinations

$R'COOSiR_3$	b.p.	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20}-n_C^{20}$	γ^{20} dynes/cm	Molecular Weight		Analysis			
									Ester number		Si (in %)	
							Calculated	Found	Calculated	Found	Calculated	Found
$CH_3COOSi(C_2H_5)_3$*	173.4*	760	0.8926	1.4190	0.0080	24.45	174.31	171.1; 172.3	321.32	319.0; 317.2	16.10	15.97; 15.95
$CH_3CH_2COOSi(C_2H_5)_3$	189.1	760	0.8918	1.4220	0.0079	25.54	188.34	185.9; 184.4	297.38	293.8; 290.0	14.90	14.79; 14.62
$CH_3(CH_2)_2COOSi(C_2H_5)_3$*	207.8	760	0.8869	1.4252	0.0082	25.00	202.37	200.3; 199.4	276.76	273.8; 276.6	13.86	13.68; 13.65
$(CH_3)_2CHCOOSi(C_2H_5)_3$	200.0	760	0.8790	1.4209	0.0076	24.32	202.37	200.0; 198.4	276.76	271.9; 271.7	13.86	13.79; 13.68
$CH_3(CH_2)_3COOSi(C_2H_5)_3$	225.9	760	0.8812	1.4280	0.0080	26.27	216.39	214.4; 216.8	258.82	255.9; 253.4	12.96	12.84; 12.93
$(CH_3)_2CHCH_2COOSi(C_2H_5)_3$**	219.1	760	0.8781	1.4260	0.0078	24.93	216.39	213.4; 213.8	258.82	256.3; 251.3	12.96	12.79; 12.76
$CH_3(C_2H_5)CHCOOSi(C_2H_5)_3$	218.3	760	0.8786	1.4260	0.0083	25.40	216.39	214.4; 214.2	258.82	256.1; 253.0	12.96	12.67; 12.68
$(CH_3)_3CCOOSi(C_2H_5)_3$	205.4	760	0.8683	1.4200	0.0075	23.80	216.39	214.2; 213.8	258.82	256.8; 255.1	12.96	12.80; 12.76
$CH_3(CH_2)_4COOSi(C_2H_5)_3$	241.6	760	0.8799	1.4309	0.0078	25.96	230.42	228.5; 227.0	243.06	241.9; 239.3	12.18	11.96; 11.95
$C_6H_5CH_2COOSi(C_2H_5)_3$	139.5—141.0	8	0.9872	1.4875	0.0126	28.78	250.41	249.1; 247.6	223.66	220.3; 224.4	11.20	11.03; 10.96
$C_6H_5COOSi(C_2H_5)_3$	133.0	8	0.9881	1.4930	0.0139	31.58	236.38	233.5; 233.3	236.93	236.0; 233.2	11.87	11.70; 11.66
$CH_3(CH_2)_3COOSi(C_3H_7)_3$	120.0—120.5	6	0.8726	1.4350	0.0078	25.77	258.47	255.9	216.68	214.4; 214.3	10.86	10.70; 10.69
$(CH_3)_2CHCH_2COOSi(C_3H_7)_3$	114.0—114.5	6	0.8704	1.4331	0.0081	25.26	258.47	253.5	216.68	214.4; 212.2	10.86	10.68; 10.66
$CH_3(C_2H_5)CHCOOSi(C_3H_7)_3$	112.0—112.5	5	0.8715	1.4330	0.0077	25.62	258.47	253.6	216.68	214.0; 213.0	10.86	10.65; 10.62
$(CH_3)_3CCOOSi(C_3H_7)_3$	100.0 101.0	5	0.8643	1.4291	0.0079	24.56	258.47	256.9	216.68	214.3; 216.7	10.86	10.77; 10.72
$CH_3(CH_2)_3COOSi(C_4H_9)_3$	143.5—144.0	5	0.8710	1.4400	0.0072	26.94	300.54	299.5	186.34	184.9; 185.6	9.33	9.20; 9.17
$(CH_3)_2CHCH_2COOSi(C_4H_9)_3$	140.0—140.5	5	0.8661	1.4390	0.0080	26.50	300.54	298.6	186.34	184.1; 183.0	9.33	9.12; 9.20
$CH_3(C_2H_5)CHCOOSi(C_4H_9)_3$	139.5—140.0	5	0.8668	1.4389	0.0078	26.65	300.54	296.6	186.34	184.7; 185.1	9.33	9.14; 9.23
$(CH_3)_3CCOOSi(C_4H_9)_3$	129.5	5	0.8623	1.4350	0.0081	25.65	300.54	296.3	186.34	184.9; 183.7	9.33	9.16; 9.23

* Previously described [16, 18, 24].

** Previously described [9].

made of heat resistant glass, supplied with a reflux condenser and a thermometer. The upper end of the condenser was connected with a Tishchenko bottle with concentrated sulfuric acid and then with a gasometer to collect the hydrogen. 0.2 mole of the corresponding acid was placed in the reaction flask, after which a powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and, finally, 0.1 mole of trialkylsilane was introduced. After this, the reaction mixture was heated until hydrogen evolution ceased and was distilled over powdered copper to eliminate the elementary iodine. The trialkylacyloxysilane thus isolated was then purified by fractional distillation.

We present the description of several synthesis as examples.

Synthesis of triethylacetoxysilane

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine was added to 12.0 g (0.2 mole) of acetic acid and then 11.6 g (0.1 mole) of triethylsilane was added. The reaction mixture was boiled until the hydrogen evolution completely ceased, which required 2.5 hours. In the course of this period, 2.6 liters of hydrogen was evolved, while the boiling point of the mixture rose to 174°. By distilling the reaction mixture over powdered copper, 6.1 g of acetic acid with a b.p. of 118.0-119.0° (755 mm) and 15.0 g of triethylacetoxysilane with a b.p. of 172.0-173.2° (755 mm) were obtained. After a second fractional distillation, the triethylacetoxysilane had a b.p. of 173.2° (754.7 mm) and had the constants presented in Table 2.

On conducting the reaction of triethylsilane with acetic acid in the presence of iodine as the catalyst, the yield of triethylacetoxysilane amounted to 69% under analogous conditions, while in the presence of sulfuric acid it amounted to 30% of the theoretical. Triethylsilane does not react with acetic acid in the presence of anhydrous aluminum chloride.

Synthesis of triethyltrimethylacetoxysilane.

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and then 11.6 g (0.1 mole) of triethylsilane was added to 20.4 g of trimethylacetic acid. In 2-3 minutes after mixing the components, the reaction mixture spontaneously became heated to 130°, and hydrogen was evolved.

The reaction mixture was then periodically (every 10-15 minutes) heated until the hydrogen evolution completely ceased, which required 1.5 hours. After this period, 2.5 liters of hydrogen had been evolved and the temperature of the reaction mixture had risen to 208°. A repeated fractional distillation of the reaction mixture gave 10.3 g of the initial trimethylacetic acid with a b.p. of 163.0-164.2° (759 mm) and 14.0 g of triethyltrimethylacetoxysilane with a b.p. of 204.0-205.5° (759 mm), i.e., 87.8% of the theoretical.

Synthesis of Triethylbenzooxysilane

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and then 11.6 g (0.1 mole) of triethylsilane was added to 24.4 g (0.2 mole) of fused benzoic acid. After heating the reaction mixture for 1.5 hours, its temperature had risen to 265°; at the same time, 2.3 liters of hydrogen had been evolved. By vacuum distilling the reaction mixture, 9.0 g of the initial benzoic acid with a b.p. of 118-119° (5 mm) and 23 g of the crude triethylbenzooxysilane with a b.p. of 132-133° (8 mm), containing free benzoic acid, were obtained. After purification from the admixture of benzoic acid by freezing out, the triethylbenzooxysilane was again fractionally distilled in a vacuum, after which it had a b.p. of 133.0° at 8 mm.

Freezing out in the purification of triethylphenylacetoxysilane from admixture of phenylacetic acid was used in the same way.

Synthesis of tri-n-butylisovaleroxysilane

20.4 g (0.2 mole) of isovaleric acid, 0.1 g of aluminum, 1.5 g of iodine and 20.0 g (0.1 mole) of tri-n-butylsilane were heated while being constantly stirred until evolution of hydrogen ceased, which took 1 hour. 2.4 liters of hydrogen was evolved under these conditions. After distilling off the valeric acid, 5.3 g of which came over at 175-176°, the residue was vacuum distilled. 12.9 g of tri-n-butylisovaleroxysilane with a b.p. of 140.0-140.5° (5 mm), i.e., 85.9% of the theoretical, was obtained as a result.

Synthesis of triethylacetoxysilane by the reaction of triethylsilane with mercury acetate.

11.6 g (0.1 mole) of triethylsilane was added to 31.9 g (0.1 mole) of anhydrous mercury acetate. The mixture became spontaneously heated to 86°. Upon further heating of the mixture for 40 minutes on an air bath, the boiling point of the mixture rose to 175°. Drops of metallic mercury formed on the bottom of the reaction flask. No gas evolution was observed during the reaction. The liquid reaction products were filtered off from the mercury

TABLE 3

Constants of the Initial Acids Used in the Syntheses of the Trialkylacyloxysilanes

Acid	B.p. at 760 mm	n_D^{20}	Literature data [30]		Notes	
			B.p. at 760 mm	n_D^{20}	Our data	Literature Data [30]
HCOOH	101.1	–	100.75	–	d_4^{20} 1.2206	d_4^{20} 1.22036
CH_3COOH	117.9	1.3740	118.1	1.37151	—	—
CH_3CH_2COOH	140.7	1.3867	141.22	1.38623	—	—
$CH_3CH_2CH_2COOH$	163.7	1.3980	164.05	1.39796	—	—
$(CH_3)_2CHCOOH$	154.4	1.3941	154.70	1.39300	—	—
$CH_3(CH_2)_3COOH$	185.6	1.4090	186.35	1.40800	—	—
$(CH_3)_2CHCH_2COOH$	176.4	1.4033	176.5	1.40331	—	—
$C_2H_5CH(CH_3)COOH$	176.5	1.4060	177.0	1.4051	d_4^{20} 0.9361	—
$(CH_3)_3CCOOH$	163.7-163.9	—	163.7-163.8	—	M.p. 35.5-35.7°	M.p. 35.3-35.5°
$CH_3(CH_2)_4COOH$	204.0	1.4170	205.15	1.4170	—	—
$C_6H_5CH_2COOH$	126.5-127.1 (5 mm)	—	144.5 (12 mm)	—	M.p. 76.6°	M.P. 76.5°
C_6H_5COOH	118.7-119.3 (5 mm)	—	—	—	M.p. 122.0°	M.p. 122.305°

and its salts, which were then washed with ether. The filtrate was fractionally distilled after preliminary elimination of the ether. 5.4 g of acetic acid with a b.p. of 118-120° (758) mm) and 12.7 g of triethylacetoxysilane with a b.p. of 172-174° (758 mm) were thereby obtained. The yield of triethylacetoxysilane amounted to 72.5% of the theoretical. After a repeated fractional distillation, it had a b.p. of 173.3° (752.1 mm); d_4^{20} 0.8925; n_D^{20} 1.4190.

Found%: Si 15.82, 15.86; ester number 318.5, 317.2; $CH_3COOSi(C_2H_5)_3$. Calculated %: Si 16.10; ester number 321.3.

Literature data for triethylacetoxysilane: Ladenburg [18] – b.p. 168°; d_0^0 0.9039; Sommer and others [24] – b.p. 167° (726 mm).

The physical constants of the triethylacetoxysilane obtained are in excellent agreement with the constants of this compound which we obtained by the reaction of triethylsilane with acetic acid (Table 2). This indicates that the triethylacetoxysilane, obtained by the methods described previously [18,24], apparently contained an admixture, since it had a boiling point 5-6° lower. *

SUMMARY

A new method for the synthesis of trialkylacyloxysilanes by the reaction of trialkylsilanes with organic acids in the presence of catalyst was worked out. 19 compounds of this type, 16 of which had not been known previously, were synthesized by this method in a yield of 81-87%, and their physical properties were determined. It was found that the course of the reaction of trialkylsilanes with carboxylic acids is only slightly dependent on the structure of the trialkylsilane and acid. A scheme for the mechanism of the reaction was proposed. It was shown that trialkylacyloxysilanes can also be prepared by the reaction of trialkylsilanes with mercury salts of carboxylic acids.

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* Larsson [16], in a work which recently became accessible to us, gives a b.p. of 175-177° for triethylacetoxysilane.

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SYNTHESIS AND PROPERTIES OF HEXAPHENYLDISILAZANE AND HEXA-p-TOLYLDISILAZANE

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The conditions for preparing the sole hexaaryldisilazane which is known in the literature – hexaphenyldisilazane–were indicated in the work of Reinolds and his coworkers [1]; they synthesized it by the reaction of triphenylsilane with liquid ammonia in the presence of metallic sodium. According to the data of the authors [1], this compound consists of a crystalline substance with a m.p. of 175°.

In the present work, we describe a method for preparing hexaaryldisilazanes which consists in passing gaseous ammonia into a solution of triarylfluorosilane in toluene which is heated to 100-110° in the presence of metallic lithium. Thus, for example, we obtained as a result of the reaction of triphenylfluorosilane with ammonia in the presence of lithium, crystalline hexaphenyldisilazane which was insoluble in ethyl ether, petroleum ether and ethyl alcohol, and had a m.p. of 235-236°, and not 175° as the authors [1] reported. It is pertinent to mention that its hexaphenyldisiloxane has a m.p. of 220°. [2].

The reaction of triphenylfluorosilane under the indicated conditions proceeds in the initial stages with the formation of unstable intermediate N-lithium-containing compounds which then, reacting with the initial substance, in the end yield the rather stable hexaphenyldisilazane.

The course of the reaction is represented by the following equations

$$NH_3 + Li = NH_2Li + 1/2\,H_2$$

$$(C_6H_5)_3SiF + NH_2Li = (C_6H_5)_3SiNH_2 + LiF;$$

$$(C_6H_5)_3SiNH_2 + Li = (C_6H_5)_3SiNHLi + 1/2\,H_2;$$

$$(C_6H_5)_3SiNHLi + (C_6H_5)_3SiF = (C_6H_5)_3SiNHSi(C_6H_5)_3 + LiF.$$

Starting with tri-p-tolylfluorosilane [3] under the same conditions, we also synthesized hexa-p-tolyldisilazane–a crystalline substance with a m.p. of 225-226° (after recrystallization from toluene). Its analog–hexa-p-tolyldisiloxane–melts at 223° [4].

Attempts to prepare hexa-α-naphthyldisilazane, starting from tri-α-naphthylfluorosilane, gaseous ammonia and metallic lithium under analogous conditions, were not successful. Tri-α-naphthylaminosilane [5], which melted at 204-206°, was isolated in place of the expected product.

It should be noted that, depending on the spatial structure of the radicals directly bound to the silicon atom, the hydrogen atoms in the amino group can be replaced either by two or three silyl groups or by only one, forming the corresponding nitrogen-containing silicoorganic compounds. Thus, for example, even in the cold, chlorosilane readily reacts with ammonia, completely replacing the hydrogen atoms with silyl groups to give trisilazane [6] according to the equation

$$3H_3SiCl + 4NH_3 = (H_3Si)_3N + 3NH_4Cl,$$

while the reaction of trimethylchlorosilane with ammonia leads only to the formation of hexamethyldisilazane [7]. The participation of an alkali metal is still indispensable for the preparation of hexaphenyldisilazane and hexa-p-tolyldisilazane.

EXPERIMENTAL

Hexaphenyldisilazane $(C_6H_5)_3SiNHSi(C_6H_5)_3$

In a side-arm flask, equipped with a reflux condenser, 0.025 mole (6.96 g) of triphenylfluorosilane with a m.p. of 63-64°, dissolved in 50 ml of toluene and 0.1 mole of metallic lithium, cut in the form of fine flakes, were introduced. Then, while the toluene was being heated to weak effervescence, gaseous ammonia, dried over CaO and KOH, was passed into the solution for 6 hours. After some time had elapsed, the gradual formation of a flocculent precipitate of lithium fluoride was observed in the solution; at the same time, the surface of the metallic lithium remained shiny at the end of the experiment. After cessation of the ammonia delivery, the solution was boiled for 1 hour more to complete the reaction, and then the precipitate was filtered off while hot. 4.2 g (in a yield of 32%, calculating on the basis of the initial triphenylfluorosilane) of hexaphenyldisilazane which melted at 235-236°, was isolated from the filtrate after two crystallizations from toluene. The product was practically insoluble in ethyl ether and in petroleum ether and alcohol. A mixed sample with hexaphenyldisilazane with the tetraphenylsilane [3] previously prepared by us which melted at approximately the same temperature, displayed a strong melting point depression; the mixture melted over a broad temperature range at 205-210°.

Found %: Si 10.1, 10.3; N (by Dumas' method) 2.22, 2.30; M 522, 528. $C_{36}H_{31}Si_2N$. Calculated %: Si 10.6; N 2.26; M 534.

Hexa-p-tolyldisilazane $(n\text{-}CH_3C_6H_5)_3SiNHSi(C_6H_4CH_3\text{-}n)_3$ was prepared analogously from 0.025 mole of tri-p-tolylfluorosilane with a m.p. of 103-104° and 0.1 mole of lithium. The crystals which separated from the filtrate were again recrystallized from toluene. 3.6 g (23%) of hexa-p-tolyldisilazane, which melted at 223-224°, was collected.

Found %: Si 8.6, 8.7; N (by Dumas' method) 2.60, 2.42; M 613, 606. $C_{42}H_{43}Si_2N$. Calculated %: Si 9.0; N 2.62; M 617.9.

SUMMARY

A convenient method for preparing hexaphenyl- and hexatolyldisilazanes was found and a scheme for their formation was proposed. Hexa-p-tolyldisilazane was synthesized for the first time. The melting point of hexaphenyldisilazane was determined accurately.

Hexa-α-naphthyldisilazane is not formed under the indicated conditions on account of spatial complications.

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* See Consultants Bureau Translation, p. 761.

** See Consultants Bureau Translation, p. 811.

DIPOLE MOMENTS AND STRUCTURE OF CERTAIN SULFANILAMIDE COMPOUNDS

Z. V. Pushkareva and Z. Yu. Kokoshko

The problems of the detailed structure of sulfanilamide compounds are of indisputable interest due to the great practical significance of this group of medicinal substances [1,2].

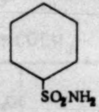
The structure of the molecules of the various sulfanilamide compounds is based on benzenesulfonamide(I).

As is well known, benzenesulfonamide derivatives acquire antibacterial, chiefly anticoccal, activity only when a primary amino group is introduced in the para position in relation to the sulfonamide group and a sulfanilamide of the general formula (III)* is formed.

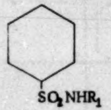
The introduction of an amino group into the meta position does not give active substances (metanilamide V). It is also known, that change in the character of R_1 in the formula (III) leads to significant changes in the activity, and sometimes to its complete suppression. Replacement of the hydrogen atoms of the benzene ring also influences the antibacterial activity (for example, the substance with formula VI).

In the present work we have attempted to elucidate the mutual dependence between such changes in structure and the values of the dipole moments of the molecules.

With this object, we measured the dipole moments of 12 substances, the majority of which we synthesized by methods described in the literature. The first group of compounds consists of substances of type (II), with various R_1 groups (the so-called deaminated sulfanilamides), viz.: (I), (VII), (VIII), (IX), (X), and (XI). The second group of substances consists of sulfanilamides of formula (III) but with the same R_1 substituents, i.e., of compounds (XII) [derived from (I)], (XIII) [derived from (IX)], (XIV) [derived from (X)] and (XV) [derived from (XI)].



(I)



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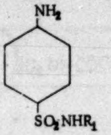

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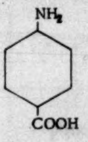

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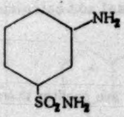

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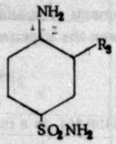

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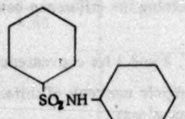

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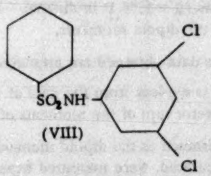

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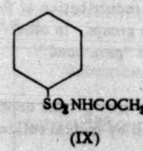

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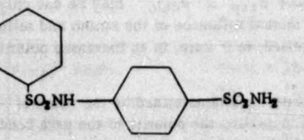
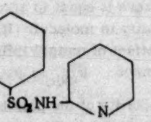


(X)



(XI)

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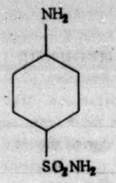
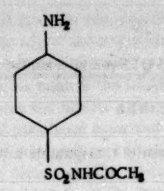
* We have in mind the sulfanilamides proper, i.e., strictly substances with a single group with a definite action mechanism, in particular, which are capable of biological competition with p-aminobenzoic acid (IV).



(XII)



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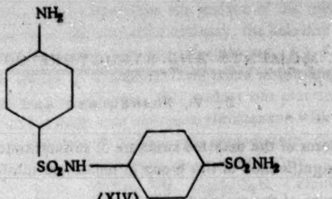

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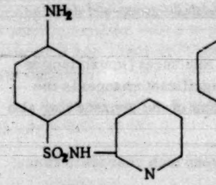

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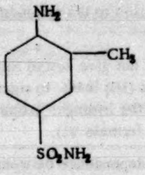
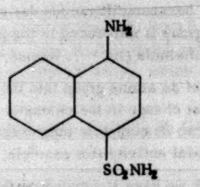
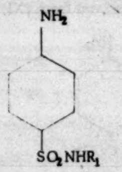


(XVI)

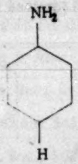


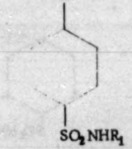
(XVII)

We then compared the dipole moments of the sulfanilamides with the moments of molecules which contain hydrogen atoms in place of the substituents; in other words, compared the following three molecules:



(III)





(II)

Such a comparison, as is well known, can be carried out via the calculation of the vector sums of the moments for sulfanilamide (III), starting from the experimental data on the dipole moments of deaminated sulfanilamides (II) and aniline (μ = 1.78 D in dioxan), and by determining the difference between the experimental and calculated values of the dipole moments.

The data obtained are presented in Tables 1, 2 and 3 for convenience.

As is evident from the data of Table 1, the dipole moments of sulfanilamides, as a rule, are greater than the simple vector sum of the moments of the substituent groups.

Inasmuch as the dipole moments of the $-NH_2$ and $-SO_2NH_2$ groups, on the basis of which the vector sums were calculated, were measured experimentally under identical conditions, while the dipole moment of unsubstituted benzene is equal to zero, the difference $\mu_{exp.} - \mu_{calc.}$ may be due only to the redistribution of the electron density in molecule (III) due to the mutual influence of the amino and sulfonamide groups. In other words, this effect of mutual influence is expressed, as it were, in an increased polarity of the "para bond" (increased, since $\mu_{exp.} - \mu_{calc.}$ is positive).

The polarity of the para bond is quantitatively characterized by the value of $\mu_{exp.} - \mu_{calc}$ and depends on the structure of R_1. The greatest effect of increasing the polarity of the para bond, caused by mutual influence of the para substituents, occurs when R_1 is a highly polar group with a plane structure.

The indicated effect of mutual influence of the amino and sulfonamide groups through the benzene ring is, as is evident, specific for para substitution and does not occur with meta substitution (No. 5 in Table 1, $\mu_{exp.} - \mu_{calc.} = 0$.

Substitution in the benzene ring [compounds (XVI) and (XVII)] leads to the reverse effect – to a lowering of the polarity of the para bond, which follows from the data of Table 2.

TABLE 1

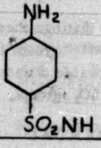
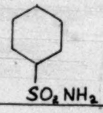
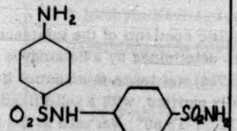
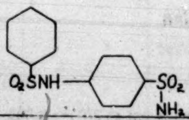
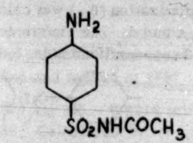
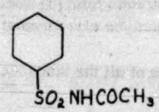
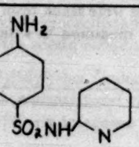
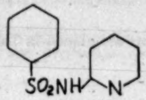
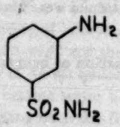
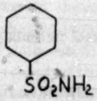
Expt. No.	Sulfanilamide		Deaminated sulfanilamide		Vector sum of the moments for the sulfanilamide ($\hat{\mu}_{calc.} \cdot 10^{18}$).	$\mu_{exp.} - \mu_{calc.}$
	Structure	Experimental dipole moment ($\mu_{exp.} \cdot 10^{18}$)	Structure	Experimental dipole moment, ($\mu_{exp} \cdot 10^{18}$)		
1		6.60		5.09	5.85	0.75
2	 NH2 O2SNH SO2NH2	6.99	 O2SNH SO2 NH2	5.55	6.13	0.86
3	 NH2 SO2NHCOCH3	6.88	 SO2NHCOCH3	4.96	5.40	1.39
4		7.2		4.95	5.7	1.5
5		5.63		5.09	5.64	0.0

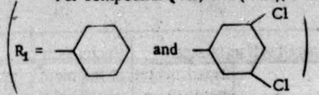
TABLE 2

Expt. No.	Substance	$\mu_{exp.} - \mu_{calc.}$
1	Sulfanilamide (XII)	0.75
2	3-Methylsulfanilamide (XVI)	0.16
3	Naphthionamide (XVII)	0.62

TABLE 3

Formula No.	$\mu_{calc.} \cdot 10^{18}$			$\mu_{exp.} \cdot 10^{18}$
	Configuration "A"	Configuration "B"	Free rotation	
(VII)	5.05	5.51	5.79	5.07
(VIII)	4.87	6.9	5.80	4.75

For compounds (VII) and (VIII), in which R_1 is comparatively simple as regards the structure of the substituent



, the method of vector sums was used to calculate the dipole moments for configurations "A" and "B" and for the free rotation of NHR in relation to the S—N bond (Fig. 1). The data presented in Table 3 were obtained as a result.

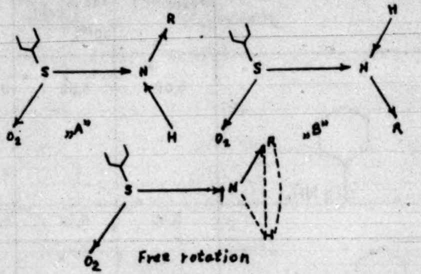


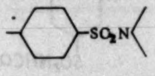
Fig. 1

It follows from these data that configuration "A", illustrated by a model of compound (VIII) (see fig. 2, p.931) is the most probable configuration.

This configuration is distinguished by the fact that the hydrogen of the —NH— groups is found at the shortest of all the possible distances from the oxygen atoms of the $-SO_2$ groups.

EXPERIMENTAL

The dielectric constants of the substances investigated (ϵ) were determined by a heterodyne method. Benzene (ϵ_{5}^{25} 2.2714) was taken as a control liquid. Dioxan, carefully purified, with a solidification temperature of 11.77-11.80°, was used as the solvent. All the determinations were carried out at 25° ± 0.02°. The density of the solutions (d) was determined, with the use of a torsion balance, at the same time as the dielectric constant. Complete polarization (P_∞) was calculated by the formula of Debye in Hoderstrand's form [3] from the experimental data for ϵ and d. The electronic polarization (P_e) was calculated from the experimental values of the refraction of benzenesulfonamide, found by Guryanova [4], since the molecules of all the substance investigated contain the



group (benzenesulfonamide radical). The refractions of the other groups in the atoms were taken from the literature data [5]. The atomic refraction was ignored. In the end, the dipole moments were measured to within ± 0.015-0.020 D.

The results of the measurements are placed in Table 4.

Substances

The substances of the general formula (III) were prepared by the condensation of acetaminobenzenesulfonyl chloride with the corresponding amines in a pyridine solvent. The acetyl derivatives obtained were then saponified to the free amine.

The deaminated products of the general formula (II) were prepared by the condensation of benzenesulfonyl chloride with the amines.

The substances were purified by crystallization from water or ethyl alcohol.

N-Phenylbenzenesulfonamide (VII). It was prepared by the condensation of pure benzenesulfonyl chloride with aniline purified, by crystallization from aqueous alcohol, to a constant melting point which was in accord with the literature data (109-110°).

N-3,5-Dichlorophenylbenzenesulfonamide (VIII). It was prepared by the condensation of benzenesulfonyl chloride with 3,5-dichloroaniline. The latter was synthesized from p-nitroaniline by the method described [6]. 9.5 g of dichloroaniline was dissolved in 54 ml of dry pyridine bases and a solution of 12 g of benzenesulfonyl chloride in 40 ml of acetone was added to the solution while it was being stirred. The mixture was stirred for 1 hour and diluted with cold water. The precipitate was filtered off, dissolved in 1 N NaOH, and the solution was acidified with hydrochloric acid. The precipitate which settled out was filtered off and recrystallized from aqueous alcohol. The yield was 26% .

On the basis of its melting point, the product was identified as the described N-3,5-dichlorophenylbenzenesulfonamide (constant m.p. at 134-135°).

TABLE 4

Results of measurement of dipole moments.

Expt. No.	Compound	P_∞	P_e	$\mu \cdot 10^{18}$
1	Benzenesulfonamide (I)	571.39	40.13	5.09
2	N-Phenylbenzenesulfonamide (VII)	595.34	64.22	5.07
3	N-3,5-Dichlorophenylbenzenesulfonamide (VIII)	539.08	73.85	4.75
4	N-p-Sulfonamidophenylbenzenesulfonamide (deaminated disulfane) (X)	714.82	78.06	5.55
5	N-Acetylbenzenesulfonamide (deaminated sulfacil) (IX)	558.14	49.37	4.96
6	N-(α-Pyridyl)-benzenesulfonamide (deaminated sulfidine) (XI)	573.51	65.76	4.95
7	Sulfanilamide (XII)	—	—	6.60
8	3-Methylsulfanilamide (XVI)	808.14	48.27	6.06
9	Naphthionamide (XVII)	943.94	61.09	6.53
10	N'-Acetylsulfanilamide (sulfacil) (XIII)	1030.45	58.80	6.88
11	N'-(α-Pyridyl)-sulfanilamide (sulfidine) (XV)	1189.56	69.08	7.2
12	N'-p-Sulfonamidophenylsulfanilamide (disulfane)	1090.78	82.58	6.99

N-p-sulfonamidophenylbenzenesulfonamide (X) (deaminated disulfane) . It was prepared by the condensation of streptocidin with benzenesulfonyl chloride in an aqueous medium. It was purified by recrystallization from water and alcohol and melted at 148°.

5.320 mg sub.: 0.4214 ml N_2 (17°, 734 mm). 3.985 mg sub.: 0.3332 ml N_2 (24°, 737 mm). Found %: N 9.0, 9.32. Calculated %: N 9.30.

N-Acetylbenzenesulfonamide (IX) (deaminated sulfacil) ; It was prepared by the acetylation of benzenesulfonamide with acetic anhydride. It was purified by repeated crystallization from water and alcohol (m.p. 122°).

N'-(α-Pyridyl)-benzenesulfonamide (XI) (deaminated sulfidine). It was prepared by condensing α-aminopyridine with benzenesulfonyl chloride in pyridine bases. It was purified by recrystallization from alcohol; the m.p. of 171-172° was in accord with the literature data.

3-Methylsulfanilamide (XVI). Toluidine was acetylated with acetic anhydride in the usual manner, and the acetyl-o-toluidine was chlorosulfonated with a 5-fold quantity of chlorosulfonic acid at 60-70° for 2 hours. The sulfonyl chloride of acetyl-o-toluidine was amidated with aqueous ammonia. The melting point of the unpurified amide was 202-204° and the yield 50% . The 3-methylacetylsulfanilamide obtained was added during stirring to a solution of 15 ml concentrated sulfuric acid in 50 ml of water which was heated to 80°. The mixture was heated on a boiling water bath for an hour and a half. The cooled mixture was filtered and 3-methylsulfanilamide was precipitated from the filtrate with ammonia. The latter was filtered off and recrystallized from water. The yield was 75%. The product was finally purified by 3-fold crystallization from water; the m.p. was 145-146°.

4.637 mg sub: 0.627 ml N_2 (19°, 734 mm). Found %: N 15.29. Calculated %: N 15.04

The Naphthionamide (XVII) was left by us for determination by B. G. Boldyrev. It was purified by recrystallization from alcohol to constant melting point (212°). In view of the insignificant decomposition on fusion, the purity of the product was additionally verified by analysis.

4.95 mg sub.; 0.5684 ml N_2 (23°, 735 mm). 5.28 mg sub: 0.5880 ml N_2 (21°, 749 mm). Found %: N 12.61, 12.64. Calculated %: N 12.61.

N'-Acetylsulfanilamide (IX) (sulfacil) The commercial product was subjected to 2-fold purification via the sodium salt; the m.p. was 182°.

N'-p-Sulfonamidophenylsulfanilamide (XIV) (disulfane). Commercial disulfane was purified via the sodium salt and repeatedly crystallized from water; in view of the diffuseness of the melting point, the purity of the substance was verified by analysis for nitrogen.

3.943 mg sub.: 0.440 ml N_2 (16°, 729 mm). 6.271 mg sub.: 0.726 ml N_2 (20°, 730 mm). Found %: N 12.82, 12.96. Calculated %: N 12.82.

Sulfidine (XV). The commercial product was crystallized three times from very large quantities of alcohol. The constant m.p. was 192°.

SUMMARY

1. The dipole moments of 12 substances of the sulfanilamide type were measured.

2. The presence of a specific mutual influence effect between the $-NH_2$ and $-SO_2NHR$ groups in the para position to each other, was demonstrated by comparison of the experimental dipole moments with the moments calculated by the vector addition method.

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DIPOLE MOMENTS AND THE STRUCTURE OF CERTAIN ACRIDINE DERIVATIVES

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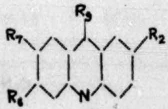
Among the derivatives of acridine (I), there is a whole series of valuable medicinal substances, including antimalarials of the atebrin (XV) type.

Inasmuch as the polarity of the molecules of medicinal substances is, in many cases, an important factor in their specific structure, in addition to the dipole moment measurements previously published [1,2], in the present work we measured the dipole moments of 12 substances which are either antimalarial compounds, or simple molecules which, however, include in themselves the structural elements of compounds of the atebrin type.

On the whole, the substances were selected in such a way that it would be possible to clarify the effect of the influence of the separate substituents on the polarity of the acridine molecule of the general formula (A). At the same time, we studied the influence on the polarity of those substituents which either cause the antimalarial activity of the acridine molecule (for example $R_2 = OCH_3$, $R_6 = Cl$, $R_9 = NHR$ and so forth), or, on the other hand, yield inactive substances (for example, $R_7 = NO_2$ and others).

The measurement of the dipole moments of substances (XIX) and (XX) was necessary for calculating the vector sums.



(A)

To clarify the influence of the separate substituents on the polarity of the acridine molecules, it was necessary to have an acridine compound with a zero dipole moment. Precisely such an acridine derivative is 9-chloroacridine, the dipole moment of which was measured by us previously [1] and proved to be equal to zero. By introducing various substituents into the molecule of 9-chloroacridine, we obtained compounds, the magnitudes of the dipole moments of which characterized the influence of the corresponding substituents on the polarity of the molecule.

The dipole moments were measured by a heterodyne method in benzene solutions at 25° and the density of the solutions was determined with the aid of a torsion balance at the same time.

The complete polarization at infinite dilution (P_∞) and the dipole moments (μ_{exp}) were calculated by the generally accepted method of Hodestrand [3]. The values of the electronic polarization (P_e) were calculated from the experimental data on the refractions. The errors in the measurements of the dipole moments amounted to ± 0.02 D.

The vector sums of the moments of the bonds ($\mu_{calc.}$) were calculated for comparison with the experimental values.

For the most part, we synthesized the substances for the investigations by the described methods, sometimes adapted, and carefully purified them by recrystallization from the corresponding pure solvents (the melting points of the substances investigated by us are presented in Table 1). Substances (V), (XV), (XVI), (XVII), (XVIII) were kindly submitted to us for the measurements by A. M. Grigorovsky.

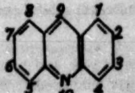
The results of the measurements and the calculations of the dipole moments are presented in Table 1.

DISCUSSION OF RESULTS

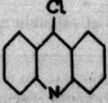
The aggregate data on the dipole moments are grouped in Table 2 according to type of substitution in the molecule of the general formula (A) for simplicity.

In discussing the data set forth in Table 2, we start from the fact that the difference between the experimental values of the dipole moments and the vector sums of the moments of the bonds appears to be a result of the mutual influence of the atoms and groups present in the molecule, and characterizes the given mutual influence effect. The following conclusions and assumptions can be drawn and made from the data of the table.

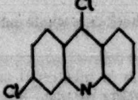
1. A methoxy group in the 2-, and a chlorine in the 6- position approximately identically increase the polarity of the 9-chloroacridine molecule. Their simultaneous presence in positions 2 and 6 does not cause a significant additional mutual influence effect ($\mu_{exp.} - \mu_{calc.} = 0.46$, 0.47 and 0.62 D respectively).


1
2
3
4
5
6
7
8
9
10
N

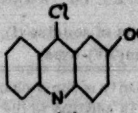
(I)



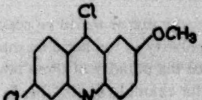
(II)



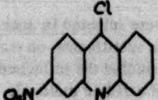
(III)



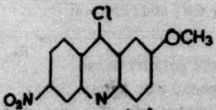
(IV)



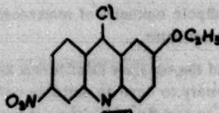
(V)



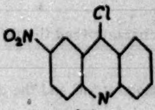
(VI)


Cl
OCH3
O2N
N

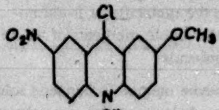
(VII)


Cl
OC2H5
O2N
N

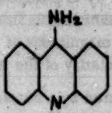
(VIII)



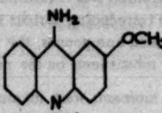
(IX)


Cl
O2N
OCH3
N

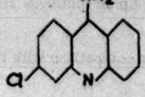
(X)



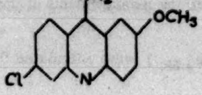
(XI)



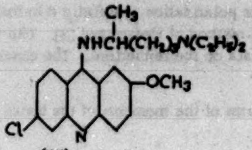
(XII)



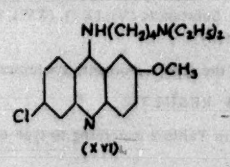
(XIII)


NH2
OCH3
Cl
N

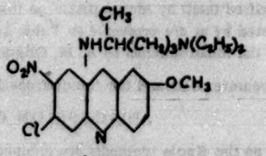
(XIV)


CH3
NHCH(CH2)3N(C2H5)2
OCH3
Cl
N

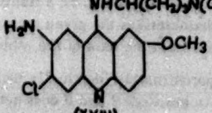
(XV)


NH(CH2)4N(C2H5)2
OCH3
Cl
N

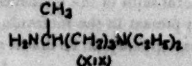
(XVI)


CH3
NHCH(CH2)3N(C2H5)2
O2N
OCH3
Cl
N

(XVII)


CH3
NHCH(CH2)3N(C2H5)2
H2N
OCH3
Cl
N

(XVIII)



$H_2N\overset{CH_3}{\overset{|}{C}}H(CH_2)_3N(C_2H_5)_2$

(XIX)

$H_2N(CH_2)_4N(C_2H_5)_2$

(XX)

TABLE 1

Formula No. in the text	Substance	M.p.	P_{∞}	P_e	$\mu_{exp.} \cdot 10^{18}$
(VI)	6-Nitro-9-chloroacridine	214°	542.54	79.54	4.98
(VII)	2-Methoxy-6-nitro-9-chloroacridine	208	893.81	84.87	6.26
(VIII)	2-Ethoxy-6-nitro-9-chloroacridine	189-191	836.85	90.25	6.01
(IX)	7-Nitro-9-chloroacridine	203-204	503.66	79.54	4.53
(X)	2-Methoxy-7-nitro-9-chloroacridine	224	621.93	87.87	5.10
(XV)	Atebrin (base)	88	806.75	131.47	5.72
(XVI)	Atebrin No. 8 (base)	78-81	847.94	128.53	5.90
(XVII)	7-Nitroatebrin (base)	–	1110.93	133.97	6.88
(XVIII)	7-Aminoatebrin (base)	–	685.33	137.91	5.16
(XX)	1-Diethylamino-4-aminopentane	–	89.50	51.08	1.36
(XXI)	1-Diethylamino-4-aminobutane	–	75.24	46.45	1.20

2. A nitrogroup in position 7, and, in particular, in position 6, markedly increases the dipole moment of the 9-chloroacridine molecule ($\mu_{exp.}$ = 4.53 and 4.98 D; $\mu_{exp.} - \mu_{calc.}$ = 0.58 and 1.03 D respectively).

A considerable mutual influence effect is manifested upon the simultaneous introduction of a methoxy or ethoxy group into position 2, and a nitro group into position 6 ($\mu_{exp.} - \mu_{calc.}$ = 1.74 and 1.46 D) and a somewhat smaller effect is manifested in 2-methoxy-7-nitro-9-chloroacridine ($\mu_{exp.} - \mu_{calc.}$ = 0.96 D).

3. 9-Amino substitution in the acridine molecule leads to a dipole moment of 4.13 D and $\mu_{exp.} - \mu_{calc.}$ = 0.85 D. The additional introduction of a methoxy group into position 2 of 9-aminoacridine and of chlorine into position 6 does not cause any particular effect, and the difference between the experimental values of the dipole moments and the vector sums is equal to 0.65 and 0.59 D respectively. With the simultaneous introduction of all three substituents (the so-called "atebrinic" type of substitution), the dipole moment is increased to 6.73 D ($\mu_{exp.} - \mu_{calc.}$ = 1.78).

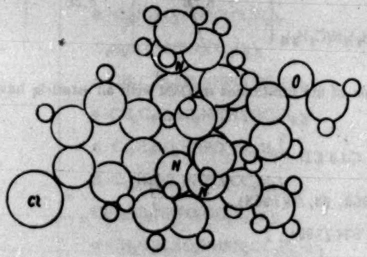


Fig. 3

4. The introduction of alkylaminoalkyl radicals into the 9-amino group, in all the cases investigated by us (XV, XVI, XVII and XVIII), leads to a lowering of the dipole moment (the solubility of the substances in benzene and their capacity to form hydrates is correspondingly sharply increased) in comparison with 2-methoxy-6-chloro-9-aminoacridine (XIV). For atebrin (XV), we calculated the vector sums of the bond moments of various molecular configurations, depending on the location of the alkylaminoalkyl "chainlet", which configurations are depicted in Figs. 1,2,4 (see plate, page 931.).

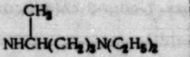
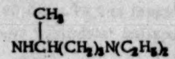
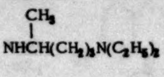
Comparison of the vector sums with the experimental values for the dipole moments permits us to assume that there is no free internal rotation of the – NHR dipole in such compounds as these, while there occurs some sort of definite steric interaction of the diethylamino groups of the diethylaminoalkyl radical with other polar groups of the atebrin molecule, which is hard to determine with only the aid of the dipole moments.

SUMMARY

1. The dipole moments of 12 substances of the acridine series were determined.

2. A comparison of the dipole moment values obtained with the corresponding vector sums of the bond moments, revealed mutual influence effect of the substituents in definite positions of the acridine ring.

TABLE 2

Formula No. in the text	R_2	R_6	R_7	R_9	$\mu_{exp.} \cdot 10^{18}$	Vector sum of the bond moments	$\mu_{exp} - \mu_{calc}$
(II)*	H	H	H	Cl	0	0	0
(III)*	H	Cl	H	Cl	2,01	1,55	0,46
(IV)*	OCH_3	H	H	Cl	1,70	1,23	0,47
(V)*	OCH_3	Cl	H	Cl	2,91	2,29	0,62
(VI)	H	NO_2	H	Cl	4,98	3,95	1,03
(VII)	OCH_3	NO_2	H	Cl	6,26	4,52	1,74
(VIII)	OC_2H_5	NO_2	H	Cl	6,01	4,55	1,46
(IX)	H	H	NO_2	Cl	4,53	3,95	0,58
(X)	OCH_3	H	NO_2	Cl	5,10	4,14	0,96
(XI)*	H	H	H	NH_2	4,13	3,28	0,85
(XII)*	OCH_3	H	H	NH_2	4,65	4,00	0,65
(XIII)*	H	Cl	H	NH_2	4,84	4,25	0,59
(XIV)*	OCH_3	Cl	H	NH_2	6,73	4,95	1,78
(XV)	OCH_3	Cl	H	 $\mathrm{NH\overset{CH_3}{\overset{\vert}{C}}H(CH_2)_3N(C_2H_5)_2}$	5,72	4,55	1,17
(XVI)	OCH_3	Cl	H	$NH(CH_2)_4N(C_2H_5)_2$	5,90	4,43	1,47
(XVII)	OCH_3	Cl	NO_2	 $\mathrm{NH\overset{CH_3}{\overset{\vert}{C}}H(CH_2)_3N(C_2H_5)_2}$	6,88	5,68	1,20
(XVIII)	OCH_3	Cl	NH_2	 $\mathrm{NH\overset{CH_3}{\overset{\vert}{C}}H(CH_2)_3N(C_2H_5)_2}$	5,16	5,28	0,12

* The results of the measurements of the dipole moments of the substances marked with an asterisk, have been presented previously by us [1].

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[1] Z. V. Pushkareva and Z. Yu. Kokoshko, Proc. Acad. Sci. USSR, 93, 77(1953).

[2] Z. V. Pushkareva and Z. Yu. Kokoshko, J. Gen. Chem., 24, 874 (1954). *

[3] Hodestrand, Z. phys. Chem 2, 428 (1929).

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* Translation page 869, this issue.

DIALKYL ESTERS OF ARYLSULFONAMIDOPHOSPHORIC ACIDS

A. V. Kirsanov and V. I. Shevchenko

Dialkyl esters of arylsulfonamidophosphoric acids were obtained by the acidic or alkaline hydrolysis of the trialkyl esters of arylsulfonimidophosphoric acids, and directly from trichlorophosphazosulfonaryls by the action of excess of sodium alcoholates [1]. The preparation of the dialkyl esters of arylsulfonamidophosphoric acids by the action of sodium alcoholates on the di-(acid chlorides) of arylsulfonamidophosphoric acids, which completely and rigorously demonstrates the structure of these esters, is described in the present work.

In comparison with trichlorophosphazosulfonaryls, the di-(acid chlorides) of arylsulfonamidophosphoric acids react considerably less energetically with sodium alcoholates. When the di-(acid chloride) of an arylsulfonamidophosphoric acid, ground to a fine powder, is added to a solution of sodium alcoholate in the corresponding alcohol, the reaction proceeds smoothly with insignificant evolution of heat. The sodium salts of the dialkyl esters are formed in excellent yields as a result of the reaction according to the scheme:

$$ArSO_2NHPOCl_2 + 3NaOAlk \longrightarrow ArSO_2NNaPO(OAlk)_2 + 2NaCl + AlkOH.$$

The formulas, yields, and melting points of the dialkyl esters of arylsulfonamidophosphoric acids thus obtained are presented in Table 1.

The dimethyl and diethyl esters crystallize well and are readily isolated from the reaction mixture in the pure state. The dibutyl esters consist of thick, viscous liquids, difficult to purify as such; therefore they were isolated and purified in the form of the characteristic sodium salts, by the decomposition of which the pure dibutyl esters were obtained.

TABLE 1

Number of the ester	Formula of the dialkyl ester	Yield (%)	M.p.
1	$C_6H_5SO_2NHPO(OCH_3)_2$	84.1	108-109°
2	o-$CH_3C_6H_4SO_2NHPO(OCH_3)_2$	86.3	145-146
3	p-$CH_3C_6H_4SO_2NHPO(OCH_3)_2$	74.8	110-111
4	α-$C_{10}H_7SO_2NHPO(OCH_3)_2$	75.2	164-165
5	$C_6H_5SO_2NHPO(OC_6H_5)_2$	80.1	111-112
6	o-$CH_3C_6H_4SO_2NHPO(OC_2H_5)_2$	83.3	97-98
7	p-$CH_3C_6H_4SO_2NHPO(OC_2H_5)_2$	78.6	105-106
8	α-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	69.0	154-155
9	β-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	79.1	161-162
10	$C_6H_5SO_2NHPO(OC_4H_9$-$n)_2$	90.2*	liquid
11	o-$CH_3C_6H_4SO_2NHPO(OC_4H_9$-$n)_2$	88.7*	liquid
12	α-$C_{10}H_7SO_2NHPO(OC_4H_9$-$n)_2$	91.8*	75-77
13	β-$C_{10}H_7SO_2NHPO(OC_4H_9$-$n)_2$	90.4*	liquid

* In the form of the sodium salts.

The dialkyl esters of the arylsulfonamidophosphoric acids, obtained from their corresponding di-(acid chlorides) can be distinguished neither in their physical, nor in their chemical properties from the dialkyl esters obtained by other methods [1]. The sodium salts of dimethyl and diethyl esters of arylasulfonamidophosphoric acids are readily soluble in water and alcohol and insoluble in nonpolar solvents. The sodium salts of the dibutyl esters of arylsulfonamidophosphoric acids are not only soluble in water and alcohol, but also in nonpolar solvents, for example, in benzene, ether and hot carbon tetrachloride and, with more difficulty, in petroleum ether. The sodium salts of the dibutyl esters are salted out from aqueous solutions even by small concentrations of sodium chloride.

The sodium salt of the dibutyl ester of α-naphthylsulfonamidophosphoric acid is somewhat different in its solubility. It readily dissolves only in hot benzene, is difficultly soluble in cold benzene and very difficultly soluble in carbon tetrachloride and in petroleum ether. Only 0.76 g of the salt dissolves at 20° in 100 ml of benzene. The sodium salts of the dibutyl esters of the other arylsulfonamidophosphoric acids are considerably more soluble in benzene.

The sodium salts of the dibutyl esters crystallize well from a mixture of benzene with petroleum ether (1:1) in the form of fine, long needles. They have comparatively low melting points (from 145 to 190°) and melt sharply in ranges of 2-3°. The sodium salts of the dibutyl esters, as well as the free esters, have an extraordinarily bitter taste.

See the experimental part relative to the hydrolysis of the dialkyl esters with hydrochloric acid in water-alcohol solutions.

The di-(acid chlorides) of the arylsulfonamidophosphoric acids have been described in the literature [2] as crystalline substances which do not have sharp melting points and begin to melt at around 110°. Actually, twice recrystallized di-(acid chlorides) when heated in a capillary, begin to melt at around 110° and do not have a sharp melting point. However, when the di-(acid chlorides) are subjected to several recrystallizations from benzene and then from carbon tetrachloride, substances are obtained with sharp melting points. The di-(acid chloride) of phenylsulfonamidophosphoric acid which has been purified in this way melts at 132-133° without decomposition. It is of interest to note that the substance, melting at 132-133°, and the substance which begins to decompose at 110°, do not differ from each other either in their external form nor in their analytical data. Evidently, there is a negligible quantity of admixture which is difficult to eliminate by crystallization and does not influence the analytical results, but causes a marked lowering of the melting point.

The di-(acid chloride) of β-naphthylsulfonamidophosphoric acid, which has not been described in the literature, was prepared similarly to the other di-(acid chlorides) of this type by the reaction of trichlorophosphazosulfon-β-naphthyl with formic acid in accordance with a method described in the literature [2]. In contrast to the di-(acid chlorides) of phenyl-, o-tolyl-, p-tolyl-, and α-naphthylsulfonamidophosphoric acids, the di-(acid chloride) of β-naphthyl-sulfonamidophosphoric acid is readily soluble in benzene.

EXPERIMENTAL

Reaction of di-(acid chlorides) of arylsulfonamidophosphoric acids with a solution of sodium methylate in methyl alcohol.

0.01 mole of the di-(acid chloride) of the arylsulfonamidophosphoric acid, carefully ground into a fine powder, was added to a solution of 0.03 g-atoms of metallic sodium (0.7 g) in 15 ml of anhydrous methyl alcohol which was cooled with running water and was being energetically stirred.

When all the di-(acid chloride) had reacted, the sodium chloride was drawn off, washed with a small quantity of methyl alcohol, and the filtrate was concentrated to dryness in a vacuum. 10 ml of 2 N H_2SO_4 was added to the dry residue and the mixture well stirred to isolate the dimethyl esters of the arylsulfonamidophosphoric acids.

The dimethyl esters precipitated either in the form of fine, well formed crystals, or in the form of a thick oily layer which, when rubbed with a glass rod, was converted into a crystalline mass. The crystalline powder was separated, washed several times with small portions of water, and dried. The melting point of the dimethyl esters thus obtained differs from the melting point of the recrystallized products by only 2-3°. A single subsequent crystallization usually gave a pure ester with a sharp melting point.

The following dimethyl esters of arylsulfonamidophosphoric acids were thus obtained. *

1. Dimethyl ester of phenylsulfonamidophosphoric acid, yield 2.23 g.

Found %: OCH_3 23.46. Equiv. ** 1.02. Calculated %: OCH_3 23.41. Equiv.1.00.

2. Dimethyl ester of o-tolylsulfonamidophosphoric acid, yield 2.41 g.

Found %: OCH_3 22.08 Equiv. ** 1.01. Calculated %: OCH_3 22.22 Equiv. 1.00.

3. Dimethyl ester of p-tolylsulfonamidophosphoric acid, yield 2.09 g.

Found %: OCH_3 22.12. Equiv.**. 1.00 Calculated %: OCH_3 22.22 Equiv. 1.00.

4. Dimethyl ester of α-naphthylsulfonamidophosphoric acid, yield 2.37 g.

Found %: OCH_3 19.61. Equiv**1.02. Calculated %: OCH_3 19.69. Equiv. 1.00

A mixed sample of the dimethyl esters obtained with dimethyl esters of the arylsulfonamidophosphoric acids, obtained by other methods [1], displayed no melting point depression.

Reaction of the di-(acid chlorides of arylsulfonamidophosphoric acids with a solution of sodium ethylate in ethyl alcohol.

The reaction of the di-(acid chlorides) of the arylsulfonamidophosphoric acids with a solution of sodium ethylate was carried out in the same way as the reaction with sodium methylate.

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* For the formulas, yields (in %) and melting points of the esters, see Table 1.

** The indicator was phenolphthalein.

The following diethyl esters of arylsulfonamidophosphoric acids were prepared.

5. Diethyl ester of phenylsulfonamidophosphoric acid, yield 2.23 g.

Found %: OC_2H_5 30.62. Equiv. **1.07. Calculated %: OC_2H_5 30.72 Equiv. 1.00

6. Diethyl ester of o-tolylsulfonamidophosphoric acid, yield 2.56 g.

Found %: OC_2H_5 29.29. Equiv **1.03. Calculated %: OC_2H_5 29.33. Equiv 1.00

7. Diethyl ester of p-tolylsulfonamidophosphoric acid, yield 2.41 g.

Found %: OC_2H_5 29.22. Equiv. ** 1.01. Calculated %: OC_2H_5 29.33. Equiv. 1.00

8. Diethyl ester of α-naphthylsulfonamidophosphoric acid, yield 2.37 g.

Found α: OC_2H_5 26.32. Equiv.** 1.02. Calculated %α OC_2H_5 26.32. Equiv. 1.00.

9. Diethyl ester of β-naphthylsulfonamidophosphoric acid, yield 2.71 g.

Mixed samples of the diethyl esters obtained, with the diethyl esters of arylsulfonamidophosphoric acids obtained by other methods [1], displayed no melting point depression.

Reaction of the di-(acid chlorides) of arylsulfonamidophosphoric acids with a solution of sodium n-butylate in butyl alcohol

0.01 mole of the di-(acid chloride) of the arylsulfonamidophosphoric acid, carefully ground into a fine powder, was added to a solution of 0.03 g-atom of metallic sodium (0.7 g) in 20 ml of anhydrous butyl alcohol at room temperature and while it was being energetically stirred. The reaction proceeded with insignificant evolution of heat. To complete the reaction, the mixture was heated for 30 minutes on a boiling water bath. The butyl alcohol was then distilled off in a vacuum on a water bath; 10 ml of water was added to the dry residue, and the mixture obtained was transferred to a separatory funnel, energetically extracted, and let stand. The sodium salts of the dibutyl esters were readily soluble in water; however in the presence of even comparatively small quantities of sodium chloride, the solution readily separated into 2 layers. The lower layer consisted of an aqueous solution, chiefly of the sodium salt of the dibutyl ester; the upper layer consisted of an aqueous solution of sodium chloride. The lower layer was poured out into a small porcelain dish and dried on a water bath. A colorless crystalline mass of the sodium salt of the dibutyl ester with a small admixture of sodium chloride was obtained in the residue.

The sodium salts of the dibutyl esters were readily obtained in the pure form by crystallization from a mixture of equal volumes of petroleum ether (b.p. 95-100°) and benzene. See the general section for the properties of the sodium salts.

The reaction of the di-(acid chlorides) of the arylsulfonamidophosphoric acids with sodium butylate was accompanied by the formation of a small quantity of by-products which had an extraordinarily unpleasant odor.

The following sodium salts were obtained:

The sodium salt of the di-n-butyl ester of phenylsulfonamidophosphoric acid was obtained in a yield of 3.35 g (90.2%). It consisted of long, fine, transparent needles, m.p. 145-147°.

0.5901 g sub.: 0.1133 g Na_2SO_4. 0.3667 g sub.: 0.0695 g Na_2SO_4. Found %: Na 6.22, 6.14. $C_{14}H_{23}O_5NSPNa$. Calculated %: Na 6.19.

The sodium salt of the di-n-butyl ester of o-tolylsulfonamidophosphoric acid was obtained in a yield of 3.42 g (88.7%). It consisted of long, fine, transparent prisms, m.p. 153-157°.

0.5091 g sub.: 0.0888 g Na_2SO_4. 0.4362 g sub.: 0.0798 g Na_2SO_4. Found %: Na 5.65, 5.92. $C_{15}H_{25}O_5NSPNa$. Calculated %: Na 5.97.

The sodium salt of the di-n-butyl ester of α-naphthylsulfonamidophosphoric acid was obtained in a yield of 3.87 g (91.8 %). The salt was very readily soluble in water, alcohol and acetone, comparatively readily soluble in hot benzene, and more poorly soluble in cold benzene. 0.76 g of the salt dissolved in 100 ml of benzene at 20°. It was difficultly soluble in ether and very difficultly soluble in petroleum ether and carbon tetrachloride. It precipitated from benzene in the form of a flocculent precipitate, which consisted of an aggregate of very minute, transparent, thin prisms, m.p. 187-189°.

0.4707 g sub.: 0.0779 g Na_2SO_4. 0.4833 g sub.: 0.0788 g Na_2SO_4. Found %: Na 5.36, 5.28. $C_{18}H_{25}O_5NSPNa$. Calculated %: Na 5.46.

The sodium salt of the di-n-butyl ester of β-naphthylsulfonamidophosphoric acid was obtained in a yield of 3.81 g (90.4 %). In contrast to the sodium salt of α-naphthyl-sulfonamidophosphoric acid, the sodium salt of the β-naphthylsulfonamidophosphoric acid was very readily soluble in benzene. It crystallized from a mixture of benzene and petroleum ether in the form of well formed prisms, m.p. 175-180°.

0.3891 g sub.: 0.0639 g Na_2SO_4. 0.4006 g sub.: 0.0668 g Na_2SO_4. Found %: Na 5.32, 5.40. $C_{18}H_{25}O_5NSPNa$. Calculated %: Na 5.46.

Preparation of the di-n-butyl esters of arylsulfonamidophosphoric acids.

0.01 mole of the sodium salt of arylsulfonamidophosphoric acid was dissolved in 30 ml of water and the solution was acidified with 15.0 ml of 2 N H_2SO_4. The viscous oily layer which separated out was washed with water and dissolved in ether. The ethereal solution was washed with water, dried with anhydrous sodium sulfate and the solvent driven off in a vacuum on a water bath. A colorless or slightly yellowish thick viscous oil was obtained in the residue. It consisted exclusively of the dibutyl ester of α-naphthylsulfonamidophosphoric acid, which readily crystallized.

The following esters were obtained in this manner:

10. Di-n-butyl ester of phenylsulfonamidophosphoric acid, yield 3.25 g (93.0 %). It consisted of a thick, viscous oil.

0.0404 g sub.: 1.365 ml N_2 (18°, 742 mm). 0.2741 g sub.: 3.90 ml 0.2046 N NaOH. 0.6401 g sub.: 9.45 ml 0.2046 N NaOH. Found %: N 3.87. Equiv.** 1.02, 1.06. $C_{14}H_{24}O_5NSP$. Calculated %: N 4.01. Equiv. 1.00.

11. Di-n-butyl ester of o-tolylsulfonamidophosphoric acid, yield 3.42 g (99.1%). It consisted of a thick viscous liquid.

0.0356 g sub.: 1.120 ml N_2 (18°, 742 mm). 0.4876 g sub.: 6.85 ml 0.2046 N NaOH. 0.7003 g sub.: 9.55 ml 0.2046 N NaOH. Found %: N 3.60. Equiv. 1.04, 1.01. $C_{15}H_{26}O_5NSP$. Calculated %: N 3.60. Equiv. 1.00.

12. Di-n-butyl ester of α-naphthylsulfonamidophosphoric acid, yield 3.59 g (89.9 %). It crystallized from petroleum ether (b.p. 95-100°) in the form of fine, well formed prisms with a m.p. of 75-77°.

0.0364 g sub.: 0.0723 g CO_2; 0.0219 g H_2O. 0.3125 g sub.: 3.90 ml 0.2046 N NaOH. Found %: C 54.23; H 6.72. Equiv.** 1.02. $C_{18}H_{26}O_5NSP$. Calculated %: C 54.14; H 6.56. Equiv. 1.00.

13. Di-n-butyl ester of β-naphthylsulfonamidophosphoric acid, yield 3.43 g (85.9%). It consisted of a thick, viscous liquid.

0.5433 g sub.: 6.30 ml 0.2046 N NaOH. 0.5027 g sub.: 6.42 ml 0.2046 N NaOH. Found: Equiv. 1.00 1.04. $C_{18}H_{26}O_5NSP$. Calculated: Equiv. 1.00.

The di-n-butyl esters of arylsulfonamidophosphoric acids were very readily soluble in alcohol, ether, acetone, benzene and carbon tetrachloride. The dibutyl esters were insoluble in water and cold petroleum ether.

TABLE 2

Formula of the ester, subjected to hydrolysis	Quantity of unhydrolyzed ester		Yield of the amide of the arylsulfonic acid		Total yield
	(In g)	(In %)	(In g)	(In %)	(In %)
$C_6H_5SO_2NHPO(OCH_3)_2$	0	0	0.28	89.2	89.2
α-$C_{10}H_7SO_2NHPO(OCH_3)_2$	0.03	4.8	0.32	77.2	82.0
$C_6H_5SO_2NHPO(OC_2H_5)_2$	0.08	13.6	0.17	54.2	67.8
α-$C_{10}H_7SO_2NHPO(OC_2H_5)_2$	0.15	21.8	0.23	55.5	77.3

Hydrolysis of the dimethyl and diethyl esters of the arylsulfonamidophosphoric acids by a water-alcohol solution of hydrochloric acid.

A mixture of 0.002 mole of the dialkyl ester of the arylsulfonamidophosphoric acid with 20 ml of a 1 N water-alcohol solution of hydrochloric acid (10 ml of 2 N aqueous solution of the acid + 10 ml of alcohol) was boiled with a reflux condenser for 24 hours. To separate the hydrolysis products, the alcohol was driven off in a vacuum and the residue was neutralized with a solution of sodium hydroxide (to a neutral reaction to phenolphthalein). The insoluble sulfamides were separated, washed with water, dried and weighed. After separating the amide, the filtrate was concentrated in a vacuum to a volume of about 5 ml and acidified with several drops of concentrated hydrochloric acid. The dimethyl and diethyl esters which had not hydrolyzed thereupon precipitated in the form of an oil which readily crystallized. The dialkyl esters were separated, washed, dried and weighed. The amides of the arylsulfonic acids and the dialkyl esters of the arylsulfonamidophosphoric acids were identified by the melting point.

The yields of hydrolysis products are presented in Table 2.

SUMMARY

1. A method for preparing the dialkyl esters of arylsulfonamidophosphoric acids from the di-(acid chlorides) of these acids and sodium alcoholates was described.

2. The dimethyl, diethyl and di-n-butyl esters of the arylsulfonamidophosphoric acids and the sodium salts of the di-n-butyl esters were prepared, and their properties were described.

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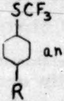
* See Consultants Bureau Translation, p. 483.

PHENYLTRIFLUOROMETHYLSULFIDES AND PHENYLTRIFLUOROMETHYSULFONES WITH SUBSTITUENTS IN THE PARA POSITION

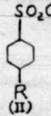
L. M. Yagupolsky and M. S. Marenets

Aromatic compounds which contain the SCF_3 and SO_2CF_3 groups have been only slightly studied [1,2]. In spite of this, they, analogously to other aromatic compounds which contain SAlk and SO_2Alk groups as substituents, may be of interest as physiologically active substances [3], insecticides [1] and intermediate products for the synthesis of dyes [2]. In the present work, we have synthesized a series of compounds of the type:



(I)

and



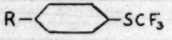
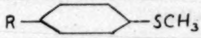
(II)

where R = Br, I, CN, COOH, $COOC_2H_5$, $CONH_2$, NH_2 * and $NHCOCH_3$.*

The substances containing the SCF_3 group were prepared by us via the chlorination of the methyl group in the p-nitrophenylmethylsulfide and replacement of the chlorine atoms in it by fluorine with the aid of antimony trifluoride. The p-nitrophenyl-trifluoromethylsulfide was reduced into the amine [2]. The amino group was replaced with other substituents by the Sandmeyer reaction.

SCF_3 derivatives differ in their physical properties from the corresponding SCH_3 derivatives. Replacement of the methyl group by the trifluoromethyl group, as in many other cases, lowers the boiling point of the compound. The specific gravity of the preparations with the SCF_3 substituent is higher than the specific gravity of the corresponding compounds with the SCH_3 group. Trifluoromethylmercapto derivatives melt lower in the majority of cases than substances which contain methylmercapto groups.

In the table we present the physical properties of compounds with the general formula (I) and, for comparison, the data on the physical properties of the corresponding para-substituted methylphenylsulfides which are presented in the literature.

R						
	Temperature		Specific gravity	Temperature		Specific gravity
	M.p.	B.p.		M.p.	B.p.	
H	–	141-142° [1]	d_4^{20} 1.2661	–	189-190° [4]	d_4^{20} 1.0576 [5]
Br	–	190-191	d_4^{22} 1.6463	37° [4]	255 [4]	d_4^{39} 1.4584 [5]
I	–	86-87 at 10 mm	d_4^{22} 1.8677	38 [6]	—	—
OH	57-58°	—	—	84-85 [7]	—	—
CN	40-41	—	—	64 [6]	—	—
COOH	160-161	—	—	192 [6]	—	—
$COOC_2H_5$	—	96-97 at 5 mm	d_4^{25} 1.2752	28 [8]	168 [8] at 15 mm	—

The trifluoromethylmercapto group is stable and resistant to the action of acids and alkalis. Thus, when p-cyanophenyltrifluoromethylsulfide is saponified with concentrated hydrochloric acid in a sealed tube at 130-140° for 6 hours, the SCF_3 group is not decomposed.

In contrast to the CF_3 group in p-hydroxybenzotrifluoride [9], the SCF_3 group in p-hydroxyphenyltrifluoromethylsulfide is not changed by the action of a 2 N solution of alkali in the cold or upon heating.

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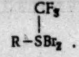
* The p-amino- and p-acetylaminophenyltrifluoromethylsulfides were described by one of us and A. I. Kiprianov in a previous work [2].

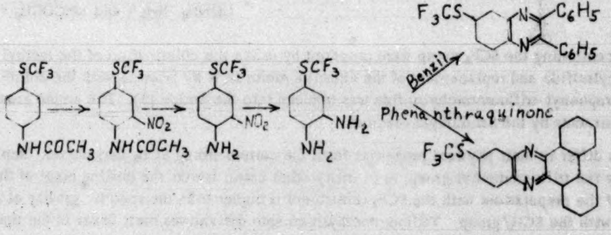
In the SCF_3 radical, the electrons are drawn off from the sulfur atom by the electronegative trifluoromethyl group. This, apparently, explains the fact that, in contrast to phenylmethylsulfide and its derivatives, compounds which contain SCF_3 as a substituent do not add molecules of chlorine or bromine with the formation of the stable grouping



$R\overset{CF_3}{\overset{|}{-}}SBr_2$.

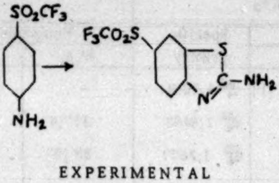
This same fact probably also explains why p-nitrophenylmethylsulfide dissolves in concentrated sulfuric acid with the formation of a reddish-violet solution [10], while p-nitrophenyltrifluoromethylsulfide gives a yellow colored solution when dissolved in concentrated sulfuric acid.

p-Acetylaminophenyltrifluoromethylsulfide was treated with a nitrating mixture; under these conditions the nitro group was located in the ortho position to the acetylamino group. After saponification of the acetyl group and reduction of the nitroamine into diamine, the latter, like all o-phenylenediamines, forms the corresponding derivatives of quinoxaline and phenanthrazine with benzil and phenanthraquinone:



The compounds containing the SO_2CF_3 group were prepared by oxidizing p-nitrophenyltrifluoromethylsulfide with chrome mixture, reducing the nitro group into the amino group and replacing it, by the Sandmeyer reaction, with other substituents. The SO_2CF_3 group is less resistant to the action of alkalis than the SCF_3 group. Thus, when p-hydroxyphenyltrifluoromethylsulfone is boiled for 5 minutes with dilute or concentrated alkali, the fluoride ion is detected in the solution.

2-Amino-6-trifluoromethylbenzthiazolylsulfone was obtained by the rhodanization of p-aminophenyltrifluoromethylsulfone:



EXPERIMENTAL

Phenyltrichloromethylsulfide

40 g of methylphenylsulfide was dissolved in 120 g of dry chloroform, and dry chlorine was passed through the solution while it was being cooled with ice water and illuminated with a lamp (200 W). During a period of 20 minutes, chlorine was absorbed and hydrogen chloride was not evolved. Then an abundant evolution of hydrogen chloride began. The chlorination was continued until the calculated increase in weight was obtained and then the solution was left for 1 hour at room temperature. The chloroform was distilled off. The product was vacuum distilled. The b.p. was 108-110° at 5 mm. The m.p. was 35°. The yield was 66 g (90 %).

Found %: Cl 46.63, 46.73. $C_7H_5SCl_3$. Calculated %: Cl 46.79

Phenyltrifluoromethylsulfide

32 g of phenyltrichloromethylsulfide and 32 g of sublimed antimony trifluoride were rapidly heated in a Wurtz flask until the exothermic reaction began. The phenyltrifluoromethylsulfide which formed was distilled off. The product was extracted with ether and the ethereal solution was washed with 6 N HCl and then with water and was dried. The product distilled at 140-142 (in accord with the melting point of this compound, set forth in the patent [1]), n_D^{25} 1.4619. The yield was 17.5 g (70%).

p-Aminophenyltrifluoromethylsulfide was prepared by reducing the corresponding nitro derivative [2].

p-Bromophenyltrifluoromethylsulfide. a) 5.8 g of p-aminophenyltrifluoromethylsulfide was diazotized, and the amino group was replaced with bromine in the usual way by Sandmeyer's method. The yield of a product with b.p. 190-191°; n_D^{25} 1.5126 was 4 g (52%).

Found %: S 12.70, 12.76. $C_7H_4SBrF_3$. Calculated %: S 12.46.

b) the p-bromophenyltrifluoromethylsulfide was also prepared from p-bromophenylmethylsulfide via chlorination of the methyl group and replacement of the chlorine atoms with fluorine with the aid of SbF_3.

9.1 g of p-bromophenylmethylsulfide [11] was dissolved in 45 ml of dry chloroform, and dry chlorine was passed through the solution for 1 hour. The flask was cooled with ice water. The mixture was let stand for 1 hour, at room temperature. The chloroform was distilled off. The yield of p-bromophenyltrichloromethylsulfide was quantitative–13.6 g. After crystallization from alcohol, the product melted at 78°.

Found %: S 10.39, 10.12. $C_7H_4SCl_3Br$. Calculated %: S 10.44

6.5 g of p-bromophenyltrichloromethylsulfide and 5 g of sublimed antimony trifluoride were quickly heated to boiling in a Wurtz flask. The product was distilled, extracted with ether, the ethereal solution washed with 6 N HCl, then with water, and was dried. The ether was distilled off. The product distilled at 190-191°, n_D^{25} 1.5126. The yield was 4.2 g (77.7%).

p-Iodophenyltrifluoromethylsulfide

5 g of p-aminophenyltrifluoromethylsulfide was diazotized and the amino group replaced with iodine by the Sandmeyer reaction. The yield of product was 4.3 g (55%). The b.p. was 86-87° at 10 mm, n_D^{17} 1.5588.

Found %: S 10.56, 10.80. $C_7H_4SF_3I$. Calculated %: S 10.52.

p-Hydroxyphenyltrifluoromethylsulfide

7 g of p-aminophenyltrifluoromethylsulfide was diazotized in a sulfuric acid solution. The mixture was stirred for 1 hour at room temperature until the precipitate of amine salt disappeared. The solution of diazonium salt was slowly added from a dropping funnel into a steam distillation flask. The diazonium salt was decomposed, and the phenol was simultaneously steam distilled. The distillate was saturated with sodium chloride. The phenol was extracted with ether. The ether was distilled off. The product was vacuum distilled. The b.p. was 77-78° at 7 mm, and the m.p. 57-58°. The yield was 4.9 g (70%).

Found %: S 16.47, 16.68. $C_7H_5OSF_3$. Calculated % S 16.5

The p-nitrobenzoyl derivative of the phenol melted at 81-82°.

Found %: S 9.40, 9.51. $C_{14}H_8O_4NSF_3$. Calculated %: S 9.33.

3,5-Dibromo-4-hydroxyphenyltrifluoromethylsulfide was prepared by adding bromine to a solution of the phenol in acetic acid. The solution was left overnight. The needles which precipitated were filtered and crystallized from acetic acid. The m.p. was 54-55°. The product can also be purified by sublimation.

Found %: S 8.91, 8.99. $C_7H_3OBr_2SF_3$. Calculated %: S 9.09.

p-Cyanophenyltrifluoromethylsulfide

10 g of p-aminophenyltrifluoromethylsulfide was diazotized and the amino group replaced with the nitrile group in the usual way, by Sandmeyer's method. After completion of the decomposition of the cyanide complex of the diazonium salt, the product was steam distilled and extracted from the distillate with ether. The ethereal solution was washed with 2 N sodium hydroxide and then with water. The ether was distilled off. The product was shaken with a hydrochloric acid solution of stannous dichloride. The nitrile was separated, washed with water and extracted with ether. The ethereal solution was dried, washed with alkali and water, and the ether distilled off. The product was vacuum distilled. The b.p. was 89-90° at 10 mm. After crystallization from low-boiling petroleum ether, the m.p. was 40-41°. The yield was 4.4 g (42%).

Found %: N 7.0, 7.13. $C_8H_4NSF_3$. Calculated %: N 6.9.

p-Carboxyphenyltrifluoromethylsulfide

2.4 g of p-cyanophenyltrifluoromethylsulfide was sealed in a tube with 6 ml of concentrated hydrochloric acid and heated for 6 hours at a temperature of 130-140°. After opening the tube, the product was filtered and dissolved in alkali. The alkaline solution was filtered, and the p-carboxyphenyltrifluoromethylsulfide was precipitated with hydrochloric acid. The yield was 2.26 g (83%). After crystallization from aqueous alcohol, the m.p. was 160-161°.

Found %: S 14.54, 14.61. Equiv. 220. $C_8H_5O_2SF_3$. Calculated %: S 14.42. Equiv. 221.

The acid chloride of the acid.

Obtained by heating 3 g of the acid on a water bath with a 5-fold excess of thionyl chloride for 3 hours. The thionyl chloride was distilled off. The product was vacuum distilled. The b.p. was 104-105° at 12 mm. The yield was 3 g (92%).

The ethyl ester of p-carboxyphenyltrifluoromethylsulfide;

Prepared by heating 2.4 g of the acid chloride of the acid on a water bath with 10 ml of anhydrous ethyl alcohol. The alcohol was distilled off. The product was vacuum distilled. A liquid with a pleasant odor was obtained. The b.p. was 96-97° at 5 mm, n_D^{25} 1.4812. The yield was 2.2 g (88%).

The hydrazide of the acid

Prepared by boiling the ethyl ester of the acid with hydrazine hydrate. After crystallization from aqueous alcohol, the m.p. was 124-125°

Found %: N 12.12 , 12.16. $C_8H_7ON_2SF_3$. Calculated %: N 11.86.

The amide of the acid.

Prepared from the acid chloride of the acid and aqueous ammonia. The amide was crystallized from aqueous alcohol. The m.p. was 125-126°.

Found %: N 6.44, 6.49. $C_8H_6ONSF_3$. Calculated %: N 6.34.

3-Nitro-4-acetylaminophenyltrifluoromethylsulfide.

3.6 g of p-acetylaminophenyltrifluoromethylsulfide was placed in a three-necked flask, equipped with a mechanical stirrer, a thermometer and a dropping funnel. A nitrating mixture (6 ml of HNO_3, d 1.41, and 7 ml of H_2SO_4, d 1.84), cooled to −5°, was slowly added to the acetyl derivative. The mixture was stirred for 2 hours. During and after the addition of the nitrating mixture, the temperature was kept at 2-4°. The product was poured out on ice, filtered and washed with water. The yield of crude product was 4.2 g. After crystallization from alcohol, 3.7 g (86%) of long yellow needles with a m.p. of 101-102° was obtained.

Found %: N 10.08, 9.9. $C_9H_7O_3N_2SF_3$. Calculated %: N 10.00.

3-Nitro-4-aminophenyltrifluoromethylsulfide.

3.6 g of 3-nitro-4-acetylaminophenyltrifluoromethylsulfide was boiled on a water bath with a solution of 1.2 g of potassium hydroxide in 10 ml of 75% alcohol for 15 minutes. The mixture was left overnight. The solution was diluted with water, and the product filtered and washed with water. The yield was 2.9 g (95%). After crystallization from alcohol, the m.p. was 85-86°.

Found %: N 11.82, 11.90. $C_7H_5O_2N_2SF_3$. Calculated % : N 11 76

3,4-Diaminophenyltrifluoromethylsulfide.

A solution of 10 g of stannous dichloride in 40 ml of concentrated hydrochloric acid was gradually added to a solution of 3 g of 3-nitro-4-aminophenyltrifluoromethylsulfide in 25 ml of alcohol. The temperature was kept at 50-60°. The solution was then heated for 1 hour on a water bath. The alcohol was distilled off under the vacuum created by a water jet pump. The residue was rendered alkaline with a solution of sodium hydroxide. The product was extracted with ether. The ethereal solution was dried. The ether was distilled off. The yield was 1.9 g (75%). After crystallization from aqueous alcohol, it consisted of white needles with a m.p. of 46-47°.

Found %: N 13.62 13.69. $C_7H_7N_2SF_3$. Calculated %: N 13.46.

The diacetyl derivative

Prepared from the diamine and acetic anhydride. After crystallization from alcohol, the m.p. was 190-191°.

Found %: N 9.36, 9.49. $C_{11}H_{11}O_2N_2SF_3$. Calculated %: N 9.58.

2,3-Diphenyl-6-trifluoromethylmercaptoquinoxaline.

0.2 g of 3,4-diaminophenyltrifluoromethylsulfide and 0.2 g of benzil were dissolved in alcohol and heated on a water bath. After dilution with water, the product was filtered and crystallized from aqueous alcohol. The m.p. was 140-141°. The yield was 0.25 g (66%).

Found %: N 7.48, 7.36. $C_{21}H_{13}N_2SF_3$. Calculated %: N 7.33.

2-Trifluoromethylmercaptophenanthrazine.

A solution of 0.2 g of 3,4-diaminophenyltrifluoromethylsulfide in 7 ml of alcohol was added to a warm solution of 0.2 g of phenanthraquinone in 20 ml of glacial acetic acid. After several minutes, the reaction product precipitated. The yield was 0.25 g (66%). The m.p. was 200-201°. After crystallization from alcohol, the melting point did not change.

Found %: N 7.23, 7.38. $C_{21}H_{11}N_2SF_3$. Calculated %: N 7.36.

p-Nitrophenyltrifluoromethylsulfone.

44.6 g of p-nitrophenylmethylsulfide, 28 g of CrO_3, 28 ml of H_2SO_4 and 35 ml of water were placed in a reaction vessel equipped with a mechanical stirrer, a thermometer and a reflux condenser. The mixture was stirred for 15 hours at a temperature of 120-130°. The product was steam distilled and filtered. 44.8 g of the sulfone was obtained. After crystallization from 200 ml of alcohol, the yield amounted to 41.5 g (81.3%). The m.p. of 85-86° was in accord with that set forth in the patent [1].

p-Aminophenyltrifluoromethylsulfone.

To a solution of 33 g of p-nitrophenyltrifluoromethylsulfone in 150 ml of alcohol, a solution of 120 g of $SnCl_2$ in 150 ml of concentrated hydrochloric acid was gradually added at such a rate that the temperature did not rise above 60°. The mixture was then heated for 1 hour on a water bath. The alcohol was distilled off under a water jet pump vacuum. The solution was poured out on a mixture of ice and 40% NaOH solution. The amine was extracted with ether. The ether was distilled off. The product was crystallized from alcohol. The m.p. was 96-97°. The yield was 26 g (89.3%).

Found %: N 6.3, 6.32. $C_7H_6O_2NSF_3$. Calculated %: N 6.22.

The acetyl derivative melted at 132-133°.

Found %: N 5.45, 5.5. $C_9H_8O_3NSF_3$. Calculated %: N 5.25.

p-Bromophenyltrifluoromethylsulfone.

3 g of p-aminophenyltrifluoromethylsulfone was diazotized and the amino group was replaced with bromine by the Sandmeyer reaction. The product was steam distilled. After crystallization from alcohol, the yield was 1.9 g (50%). The m.p. was 64-65°.

Found %: S 10.99, 10.75. $C_7H_4O_2SBrF_3$. Calculated %: S 11.07.

p-Iodophenyltrifluoromethylsulfone.

3 g of p-aminophenyltrifluoromethylsulfone was diazotized, and the amino group replaced with iodine, by the Sandmeyer reaction. After steam distillation, the product was crystallized from aqueous alcohol. The m.p. was 78-79°. The yield was 3 g (67%).

Found %: I 37.54, 37.88. $C_7H_4O_2SIF_3$. Calculated %: I 37.80.

p-Hydroxyphenyltrifluoromethylsulfone.

2 g. of p-aminophenyltrifluoromethylsulfone was stirred with a solution of sulfuric acid (1.5 ml of H_2SO_4 in 10 ml of water) and diazotized with sodium nitrite (0.8 g of $NaNO_2$ in 4 ml of water). Upon completion of the addition of the sodium nitrite, the mixture was stirred for 30 minutes at room temperature, and the solution was then heated until the diazonium salt was completely decomposed. After cooling, a brown precipitate settled out, which was filtered and crystallized from water. The m.p. was 119-120°. The yield was 1.16 g (58%).

Found %: S 14.23, 14.36. $C_7H_5O_3SF_3$ Calculated %: S 14.11.

The dibromide;

Prepared by adding bromine to an aqueous solution of p-hydroxyphenyltrifluoromethylsulfone. After crystallization from aqueous alcohol, the m.p. was 150°.

Found %: S 8.03, 7.95. $C_7H_3O_3SBr_2F_3$. Calculated %: S 8.3.

p-Cyanophenyltrifluoromethylsulfone.

10 g of p-aminophenyltrifluoromethylsulfone was diazotized and the amino group was replaced with the nitrile group by the Sandmeyer reaction. After complete decomposition of the cyanide complex of the diazonium salt, the

product was steam distilled and filtered. The yield was 5.2 g (50%). After crystallization from aqueous alcohol, the m.p. was 89-90°.

Found %: N 6.07, 6.13. $C_8H_4O_2NSF_3$. Calculated %: N 5.96.

p-Carboxyphenyltrifluoromethylsulfone.

2.4 g of p-cyanophenyltrifluoromethylsulfone was heated in a sealed tube with 6 ml of concentrated hydrochloric acid for 6 hours at 120-130°. After opening the tube, the acid was filtered, washed with water and crystallized from aqueous alcohol. The m.p. was 239-240°. The yield was 2.3 g (88%).

Found %: S 12.50, 12.74. $C_8H_5O_4SF_3$. Calculated %: S 12.59.

The acid chloride of the acid:

Prepared by boiling 2.3 g of the acid with 12 ml of thionyl chloride for 4 hours on a water bath. The excess thionyl chloride was distilled off and the product vacuum distilled. The b.p. was 149-150° at 20 mm, and the m.p. was 29-30°. The yield was 2 g (83%).

The ethyl ester.

Prepared by boiling the acid chloride of the acid with anhydrous ethyl alcohol. The b.p. was 148-149° at 10 mm, m.p. 47-48°.

The amide of the acid.

Prepared by two methods: 1) from the acid chloride and aqueous ammonia; m.p. 196-197° (from aqueous alcohol); 2) by saponifying the nitrile with aqueous-alcoholic alkali in the presence of hydrogen peroxide by Radziszewski's method [12]; m.p. 196-197°.

Found %: N 5.67, 5.78. $C_8H_6O_3NSF_3$. Calculated %: N 5.53.

2-Amino-6-trifluoromethylbenzthiazolylsulfone.

1.7 g of ammonium thiocyanate was added to a suspension of 2 g of p-aminophenyltrifluoromethylsulfone in 14 ml of glacial acetic acid, and while the mixture was being cooled and stirred, 1.7 g of bromine in 4 ml of glacial acetic acid was added. Upon completion of the addition of bromine, the mixture was stirred for 1 hour and left overnight. Water (60 ml) was then added and the mixture was heated to boiling, cooled and filtered. The free amine was isolated from the filtrate with soda. The product crystallized from aqueous alcohol. The yield was 1.2 g (50%). The m.p. was 220-221°.

Found %: N 9.79, 9.83. $C_8H_5O_2N_2S_2F_3$. Calculated %: N 9.93.

SUMMARY

30 compounds containing the SCF_3 and SO_2CF_3 groups as substituents in the benzene nucleus, were synthesized and their properties described.

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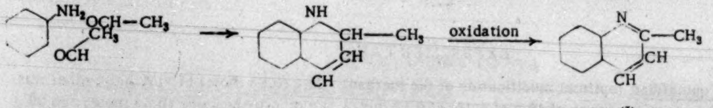
• See Consultants Bureau Translation, p. 2273.

PREPARATION OF QUINALDINE DERIVATIVES FROM AROMATIC AMINES AND VINYL ETHERS

B. A. Porai-Koshits, L. S. Efros, V. N. Vertkina and V. V. Lutsenko

Quinaldine is a valuable intermediate product which has found application in the synthesis of strong acidic and cyanine dyes. The reciprocal reaction of acetaldehyde with aniline is used at the present time to prepare it; in this reaction, quinaldine (I) is formed either directly [1] or via a stage of formation of a product of obscure structure (the so-called Schulz base [2]), which is fused by Lyashenko's method [3] with zinc chloride. The reaction in which quinaldine is formed by this method can be represented by the following scheme:



(I)

Nitrobenzene or its sulfonic acid [4] is usually used as the oxidizing agent which is necessary for the reaction. The yield of quinaldine by this method, even in the better modification of Lyashenko [3], does not exceed 50%.

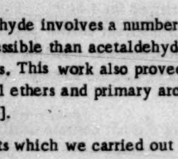
Since work with acetaldehyde involves a number of difficulties, while the vinyl ethers are at the present time in a number of cases more accessible than acetaldehyde, we determined to try to use these ethers for the synthesis of quinaldine and its derivatives. This work also proved to be interesting because up to the present time no one has studied the reaction of the vinyl ethers and primary aromatic amines, and, naturally, this question was not treated in Shostakovsky's monograph [5].

The very first experiments which we carried out involving the condensation of vinylbutyl ether with aniline in the presence of mineral acid, showed that this reaction proceeds very readily. The product obtained, after careful rectification, was identified in the form of the picrate with the picrate of known quinaldine. We then undertook to delineate the conditions for preparing quinaldine by this method, and found that there is a definite optimum acidity of the medium in which the reaction is carried out. This apparently indicates that here, just as in certain other reactions which are catalyzed by hydrogen ions [6], their role is dual: they activate the vinylbutyl ether and render the aniline passive, forming the unreactive phenylammonium ion with it.

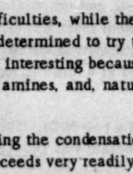
The yield of quinaldine, obtained by the optimal modification, amounts to 47-52%, i.e., does not exceed the yield of product by Lyashenko's method. However the simplicity and convenience of bringing about the reaction argues in favor of the practical value of preparing quinaldine from vinylbutyl ether.

We then attempted to use this reaction for the synthesis of quinaldine derivatives, using for this aniline which contained various substituents.

6-Methylquinaldine (II) was thereby obtained from p-toluidine; 8-methoxyquinaldine (III) from o-anisidine, while neither from p-aminophenol nor from m-phenylenediamine were quinaldine derivatives obtained; — only resinous products were formed.

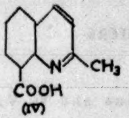


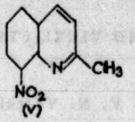
(II)

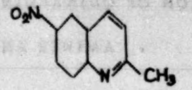


(III)

In exactly the same way, the quinaldine derivatives (IV), (V) and (VI) were obtained from anthranilic acid and from o- and p-nitroaniline, while both m-nitroaniline and 2,4-dinitroaniline proved to be incapable of entering into the condensation:


(IV)


(V)


(VI)

Thus, the reaction of aromatic amines with vinyl ethers appears to be a general method for preparing quinaldine derivatives. The success of the reaction, however, depends on the character of the substituents which are found in the nucleus. In the case of the strongly activated molecules of a reactive amine (aminophenol, m-phenylenediamine), as well as in the case of deactivation, particularly of the o-position to the amino group (m-nitroaniline), quinaldine derivatives are not obtained.

The present work fulfills a project of A. E. Porai-Koshits.

EXPERIMENTAL

Preparation of quinaldine (optimal modification of the method). 25 g (0.25 mole) of vinylbutyl ether was added in the form of drops to a mixture of 12 g of aniline (0.13 mole), 5 g of nitrobenzene (0.04 mole) and 39 g of concentrated HCl (0.4 mole) while the mixture was being stirred and heated on a boiling water bath. Upon completion of the addition of the ether, the mixture was heated for 30 minutes more and then the excess nitrobenzene was steam distilled off. The solution obtained was neutralized with 10% soda solution and the oil which was formed was extracted with 100 ml of ether. To separate the aniline [7], the ethereal solution was dried over roasted sodium sulfate, 9 g of phthalic anhydride was added, and the mixture was stirred for 1 hour. The mass was treated with 10% soda solution until the reaction of the aqueous layer was alkaline to brilliant yellow paper. The ethereal layer was separated, washed with water and dried with roasted sulfate, and the ether was distilled off at atmospheric pressure. The quinaldine which was left was distilled at 5 mm residual pressure, and the fraction which boiled at 99-101° was collected.

The yield of quinaldine was 8.2-9.3 g (44-50%). The product did not contain aniline (test with calcium hypochlorite). The melting point of the picrate was 193-194°.

Found: M 143.7 (potentiometric titration), 142 (cryometry in benzene). $C_{20}H_9N$. Calculated: M 143

6-Methylquinaldine. 6-Methylquinaldine was prepared in exactly the same way as quinaldine. After carrying out the reaction between 5.5 g of p-toluidine and 10.5 g of vinylbutyl ether in 16.5 ml of concentrated HCl, the reaction mass was neutralized with soda and the oil which was evolved was extracted with ether. The ethereal solution was treated with phthalic anhydride to separate the p-toluidine which had not reacted, and was distilled.

The oil which was obtained partially congealed on cooling; the product was separated and crystallized from ether. 6-Methylquinaldine with a m.p. of 57-59° was obtained. Its picrate had a m.p. of 178°. The literature data [8] are, respectively, 59-60° and 178°.

8-Methoxyquinaldine. 7.5 g of vinylbutyl ether was added in the form of drops to a mixture of 5.5 g of o-anisidine and 12 ml of concentrated HCl which was being heated on a water bath and being stirred. The reaction mass was kept under these conditions for 1 hour and then diluted with water and neutralized with 10% soda solution. The thick oil which precipitated was extracted with benzene; after a portion of the latter was distilled off, the colorless 8-methoxyquinaldine crystallized from the remaining solution on cooling; it melted at 123° [9] after one crystallization from benzene. The yield was 1.8 g (25%).

Quinaldine-8-carboxylic acid. 15 g of vinylbutyl ether was added in the form of drops to a mixture of 10.5 g of anthranilic acid and 24 ml of concentrated HCl while the mixture was being heated on a water bath and being stirred. The mass was kept under these conditions for 1 hour and then concentrated to dryness. The resinous residue was treated with a mixture of equal parts of alcohol and ether, after which the precipitate was dissolved in a small quantity of water. The aqueous solution was carefully neutralized with ammonia to a very weakly alkaline reaction with brilliant yellow paper as the indicator. The acid was isolated in the form of colorless needles with a m.p. of

147°, in a quantity of 3.4 g (24%). After crystallization from water, the m.p. was 154°.

6-Nitroquinaldine. 12 g of p-nitroaniline, 24 ml of concentrated HCl and 15 g of vinylbutyl ether were the starting materials for the synthesis. After neutralizing the reaction mass with soda, a yellow product was isolated which was twice reprecipitated with soda from a solution in dilute hydrochloric acid and crystallized from aqueous alcohol for purification. The yield of product with a m.p. of 165° was 7.4 g (45%).

8-Nitroquinaldine. The starting materials were 6 g of o-nitroaniline, 12 ml of concentrated HCl and 7.5 g of vinylbutyl ether. The reaction mass was diluted with water, filtered from resin and neutralized with a 10% solution of soda. A black resinous product precipitated which slowly solidified. It was separated, dissolved in concentrated HCl, the solution filtered free of contamination and neutralized with ammonia ; a yellow precipitate thereupon settled out which was crystallized from dilute alcohol. The long yellow needles of 8-nitroquinaldine melted at 139°. The yield was 3.6 g (44%).

SUMMARY

The reciprocal reaction of primary aromatic amines with vinyl ethers leads to the formation of quinaldine derivatives.

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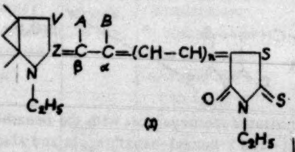
MEROCYANINE DYES DERIVED FROM RHODANINE

VI. DIMETHINEMEROCYANINES CONTAINING THE ALKYL OR PHENYL GROUP IN THE POLYMETHINE CHAIN

M. V. Deichmeister, Z. P. Sytnik, I. I. Levkoev and E. B. Lifshits

In preceding works [1,2], devoted to the investigation of merocyanine derivatives of rhodanine (I; A and B = H; n = 0 1 or 2), we studied the influence of the nature of the heterocyclic nitrogen-containing radicals and the long external polymethine chain on the properties of these dyes:

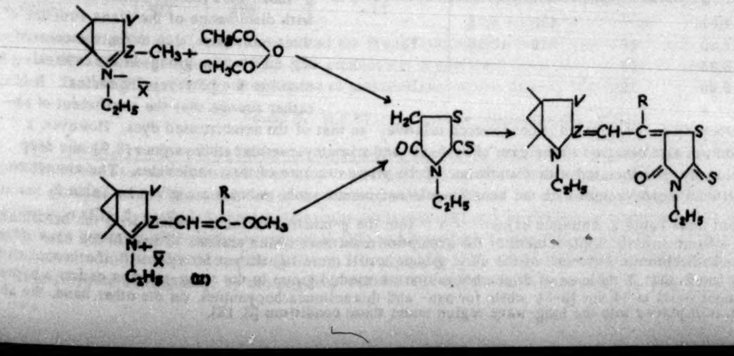

(I)

where V = O, S, Se, CH=CH, $C(CH_3)_2$, $N-CH_3$ etc.; Z = carbon or the $=CH-\overset{|}{C}=\overset{|}{C}-$ group (in the latter case the V grouping is absent); n = 0, 1 or 2.

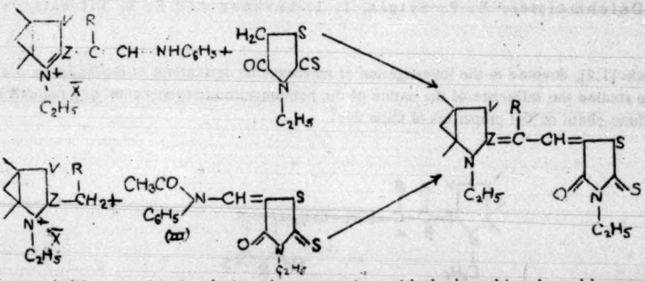
The entrance of substitutent groups into the polymethine chain of the cyanine dyes exerts a considerable influence on their color [3-12], and, depending on the character and position of the substituents, and also on the nature of the heterocyclic nitrogen-containing residue, either a bathochromic or a hypsochromic displacement of the absorption maximum can be observed.

The question of the influence of substituents in the polymethine chains of the merocyanines on their color has still been investigated very little. A number of chain-substituted merocyanines have been presented in the patent literature which have been proposed as sensitizers for silver halide photographic emulsions [13-16]. The positions of the absorption and activation maxima have been presented for certain of these dyes. A few of the works of A. van Dormael with his coworkers have been devoted to the synthesis and investigation of dimethinemerocyanines which contain various complex substituents in the meso position [17, 18]. However, it is not possible on the basis of these data to draw definite conclusions concerning the influence of the presence of substituents in the polymethine chain on the color of the merocyanines. In this connection, we synthesized a number of α- and β-alkyl- and phenyl-substituted dimethylmerocyanine derivatives of 3-ethylrhodanine (I; n = 0), which differ in the nature of the heterocyclic nitrogen-containing radicals, and investigated their absorption spectra in alcoholic solutions.

Meso-methyl substituted merocyanines with benzthiazole, benzoxazole, thiazoline, 4-phenylthiazole and 6-dimethylaminobenzthiazole radicals (I; A = H; B = CH_3) were synthesized with satisfactory yields by heating the quaternary salts of the corresponding bases, containing the methyl group in the 2 position, with 3-ethylrhodanine and acetic anhydride in pyridine (cf. [13a].


(II)

For the synthesis of meso-ethyl- and phenyl-substituted merocyanine derivatives of benzthiazole, and also of β-naphthothiazole and benzselenazole with a methyl group at the central carbon atom of the polymethine chain, the quaternary salts of 2-β-methoxy-[19, 20] or methylmercaptoalkenyl derivatives [15 a] of the corresponding bases (II) were used which were condensed with 3-ethylrhodanine in propanol in the presence of triethylamine. It was also found that in the reaction of 3-ethylrhodanine with the quaternary salts of 2-β-anilinobutenylbenzoxazole and 2-β-anilinoisobutenylbenzthiazole, the corresponding α- and β-ethyl substituted merocyanines are formed. The most satisfactory yields in these cases were obtained by carrying out the reaction in a mixture of butanol and pyridine in the presence of triethylamine.

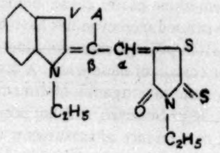


We succeeded in preparing β-substituted merocyanines with the benzthiazole and benzoxazole radicals by condensing the quaternary salts of 2-ethyl- and 2-benzyl-benzthiazole and also of 2-ethylbenzoxazole with 3-ethyl-5-acetanilinomethylenerhodanine (III) in a mixture of butanol and pyridine in the presence of triethylamine. More deeply colored salt-like dyes were formed as by-products in this reaction; they were separated by chromatographing them on aluminum oxide.

The absorption maxima and molar extinction coefficients (ε) of dimethylmerocyanines with the benzthiazole and benzoxazole radicals which contain substituents in the beta-position of the polymethine chain, are presented in table 1.

TABLE 1

General Formula:



A	V = S			V = O		
	λmax. (mμ)	ε · 10^{-4}	Displacement in comparison with the unsubstituted dye (in mμ)	λmax. (mμ)	ε · 10^{-4}	Displacement in comparison with the unsubstituted dye (in mμ)
H . .	524	11.31	–	492	8.05	–
CH_3. .	540	11.29	16	510	13.25	18
C_2H_5.	540	8.35	16	–	–	–
C_6H_5.	536	9.40	12	–	–	–

As is evident from Table 1, the entrance of alkyl groups, and also of the phenyl group into the beta position of these dyes causes a deepening of the color. The absorption coefficient remains unchanged under these conditions in the case of the thia-derivatives, or is somewhat lowered, while it is appreciably increased for dyes with the benzoxazole residue.

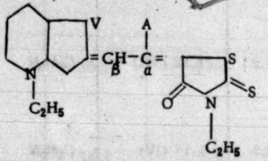
It can be assumed by analogy with the 8,10-substituted thiacarbocyanines [6] that the bathochromic displacement of the absorption maximum observed in the β-substituted merocyanines is associated with disturbance of the plane structure of their molecules, due to the closeness of the substituting groups in the external chain to the heterocyclic radical. It is rather strange that the coefficient of absorption of the merocyanines investigated is not lowered relative to that of the unsubstituted dyes. However, a similar phenomenon was also observed in the case of 8,10-di- and trimethylenethiacarbocyanines [7,9], the deep color of which, evidently, is associated with disturbance of the plane structure of their molecules. The absorption maxima of α-substituted merocyanines with the benzthiazole and benzoxazole radicals are given in Table 2.

As is evident from Table 2, entrance of substituents into the α-position of merocyanines with the benzthiazole radical causes a bathochromic displacement of the absorption maximum which reaches 18 mμ in the case of the phenyl group. The bathochromic influence of the alkyl groups is still more significant for dyes with the benzoxazole radical. It is well known that in the case of thiacarbocyanines, a methyl group in the meso-position causes a hypsochromic displacement equal to 14 mμ [3-5], while for oxa- and thiazolinocarbocyanines, on the other hand, the absorption maximum is displaced into the long-wave region under these conditions [3, 12].

From this point of view, it was of interest to investigate the α-methyl-substituted merocyanines with nitrogen-containing radicals of varying basicity. The absorption maxima of a number of α-methyl substituted merocyanines are set forth in Table 3, and are arranged in the order of increasing bathochromic influence of the methyl group. It is evident from the data of Table 3, that the entrance of a methyl group at the central carbon atom of the polymethine chain, in the case of the merocyanine with the 4-phenylthiazole radical, causes an insignificant hypsochromic displacement of the absorption maximum; as one proceeds to dyes with radicals which are less basic, this effect becomes bathochromic and increases all the more as the basicity of the nitrogenous heterocyclic radical decreases.

TABLE 2

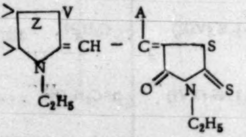
General Formula:



A	V = S		V = O	
	λmax. (in mμ)	Displacement in comparison with the unsubstituted dye (in mμ)	λmax. (in mμ)	Displacement in comparison with the unsubstituted dye (in mμ)
H	524	–	492	–
CH_3. . . .	532	8	504	12
C_2H_5	536	12	506	14
C_6H_5. . . .	542	18	–	–

TABLE 3

General formula:



Heterocyclic nitrogenous radical Z	λmax. (in mμ)		Displacement (in mμ)
	A = H	A = CH_3	
4-Phenylthiazole	538	536	−2
6-Dimethylamino-benzthiazole	553	556	+3
β-Naphthothiazole	542	548	+6
Benzselenazole	524	532	+8
Benthiazole	524	532	+8
Benzoxazole	492	512	+12
Thiazoline	482	495	+13

In the slightly basic merocyanines, the electron displacements from the nitrogen atom toward the carbonyl oxygen are evidently relatively small, as a consequence of which the electron density is irregularly distributed in their chromophore. The entrance of an electropositive methyl group at the central carbon atom of the polymethine chain of these dyes should lead to increasing of the electron displacement at the oxygen and, consequently to the equalization of the electron density in the chromophore, as a result of which deepening of the color can be expected.

When the basicity of the heterocyclic nitrogen-containing radical of the dimethinemerocyanine derivatives of rhodanine is increased, their polarity is considerably increased [1, 21-24]. In this case, the entrance of a methyl group at the central carbon atom of the polymethine chain should still more increase the polarity of the dye, and can lead to diminishing the regularity of the distribution of the electron density in the chromophore, and, in connection with this, to an intensification of the color.

The experimental data obtained by us concerning the influence of the methyl group in the meso-position of the polymethine chain of merocyanines on their color are in complete agreement with the considerations indicated above.

EXPERIMENTAL

Iodoethylate of 2-β-anilinopropenylbenzoxazole. A mixture of 2.9 g of the iodoethylate of 2-methylbenzoxazole and 3.1 g of ethylisothiopropionanilide was heated for 1 hour at 160° in a round-bottomed flask with an air condenser. The solid reaction mass was triturated with 50 ml of ethyl alcohol and the precipitate was filtered off and washed with alcohol. The yield was 2.2 g (53.5%). The m.p. was 179-181°. The product was crystallized from ethyl alcohol (1 part per 12 ml) for purification. The weight was 1.7 g. It consisted of pinkish flakes with a m.p. of 183-184°.

Found %: N 6.77. $C_{19}H_{21}ON_2I$ Calculated %: N 6.66.

The quaternary salts of the heterocyclic nitrogen-containing bases were synthesized by heating equimolecular quantities of the base and the ethyl ester of p-toluenesulfonic acid in a flask with an air condenser, equipped with a calcium chloride tube. The condition of the heating were as follows: for the ethyl-p-toluenesulfonates of 2-methylbenzthiazole (III), 2-methyl-6-dimethylaminobenzthiazole (IV) and 2-ethylbenzthiazole (V) – 4 hours at 140-145°, for the same esterates of 2-methylbenzoxazole (VI) and 2-methyl-4-phenylthiazole (VII) – 5 hours at 140-145°, and for the esterate of 2-methylthiazoline (VIII) – 1 hour at 120-125°. The ethyl-ethylsulfate of 2-benzylbenzthiazole (XV) was prepared analogously, by heating base with diethyl sulfate for 6 hours at 130°. The quaternary salts were

TABLE 4

Dye	Quantity (g)			Solvent	
	Of I or II	Of acetic anhydride	Of the quaternary salt	Formula	Quantity (in ml)
3-Ethyl-5-[3'-ethyl-4'-phenylthiazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.48 (I)	0.9	1.12 (VII)	C_5H_5N	3.5
3-Ethyl-5-[3'-ethyl-6'-dimethylaminobenzthiazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.48 (I)	0.9	1.17 (IV)	C_5H_5N	3.5
3-Ethyl-5-[3'-ethyl-4',5'-benzobenzthiazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidin-thion -(2)-one)(4) [14a]	0.19 (I)	–	0.43 (XIII)	n-C_4H_9OH	2
3-Ethyl-5-[3'-ethylbenzselenazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4) [19]	0.19 (I)	–	0.41 (XIV)	n-C_3H_7OH	1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4) [13a, 25]	3.2 (I)	6	6.98 (III)	C_5H_5N	24
3-Ethyl-5-[3'-ethylbenzoxazolinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	3.2 (I)	6	6.66 (VI)	C_5H_5N	24
3-Ethyl-5'-[3'-ethylthiazolidinyliden-2'-(α-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.64 (I)	1.2	1.2 (VIII)	C_5H_5N	5
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(α-ethyl)-ethyliden]-thiazolidinthion -(2)-one-(4) [13d]	0.57 (I)	–	1.47 (XVI)	n-C_3H_7OH	4
3-Ethyl-5-[3'-ethylbenzoxazolinyliden-2'-(α-ethyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.16 (I)	–	0.42 (X)	C_5H_5N n-C_4H_9OH	0.5 1
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(α-phenyl)-ethyliden]-thiazolidinthion -(2)-one -(4) [15a]	0.2 (I)	–	0.48 (XII)	n-C_3H_7OH	1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(β-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.36 (II)	–	0.52 (V)	C_5H_5N n-C_4H_9OH	0.5 1
3-Ethyl-5-[3'-ethylbenzoxazolinyliden-2'-(β-methyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.61 (II)	–	0.6 (IX)	C_5H_5N n-C_4H_9OH	0.8 1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(β-ethyl)-ethyliden]-thiazolidinthion -(2)-one-(4)	0.16 (I)	–	0.41 (XI)	C_5H_5N n-C_4H_9OH	0.5 1
3-Ethyl-5-[3'-ethylbenzthiazolinyliden-2'-(β-phenyl)-ethyliden]-thiazolidinthion -(2)-one-(4)*	0.9 (II)	–	1.13 (XV)	C_5H_5N n-C_4H_9OH	1.2 2.5

* The dye was purified by chromatographing it on aluminum oxide

Triethylamine (in g)	Duration of boiling (in minutes)	Yield (in%)	Quantity of ethyl alcohol for crystallization (ml/g)	Superficial form	M.p.	Analysis		
						Found content of N (in %)	Calculated	
							Empirical formula	N (in %)
–	90	30.9	500	Fine dark red needles	230-231°	7.20	$C_{19}H_{20}ON_2S_3$	7.21
–	90	24.6	100	Shiny green prisms	249-250	**	$C_{19}H_{23}ON_3S_3$	**
0.1	30	19.3	1650	Fine, dark red needles	243	7.00	$C_{21}H_{20}ON_2S_3$	6.78
0.1	30	34.2	500	Shiny, dark red prisms	202-203	6.60	$C_{17}H_{18}ON_2S_2Se$	6.84
–	90	15.4	1400	Shiny, violet prisms	217-218	7.57	$C_{17}H_{18}ON_2S_3$	7.72
–	90	28	1100	Brown needles with a green luster	222-224	7.95	$C_{17}H_{16}O_2N_2S_2$	8.11
–	120	27	230	Red prisms	187-188	9.01	$C_{13}H_{18}ON_2S_3$	8.90
0.15	10	15	100	Violet prisms	162-164	7.64	$C_{18}H_{20}ON_2S_3$	7.44
0.1	45	27.7	120	Fine red needles	165-167	7.71	$C_{18}H_{20}O_2N_2S_2$	7.77
0.12	10	25.6	70	Violet prisms	245-247	6.75	$C_{22}H_{20}ON_2S_3$	6.59
0.1	60	58	400	Violet flakes	205-207	7.70	$C_{17}H_{18}ON_2S_3$	7.72
0.22	120	34.6	250	Red needles	209-210	8.03	$C_{17}H_{18}O_2N_2S_2$	8.08
0.1	45	58	*** 37	Shiny green flakes	177-178	7.49	$C_{28}H_{20}ON_2S_3$	7.43
0.3	150	9.4	220	Dark red prisms	210-212	6.37	$C_{22}H_{20}ON_2S_3$	6.59

** Found % S 23.73%, calculated % S 23,71%.

*** Toluene

used to prepare the dyes without purification. The ethylmethylsulfates of 2-β-methoxy and β-methylmercapto-alkenyl derivatives of the heterocyclic nitrogenous bases were synthesized analogously, by heating the corresponding acyl- and thioacylmethylenic compounds with dimethylsulfate. The conditions of heating for the ethylmethylsulfates of 2-β-methoxypropenyl-β-naphthothiazole (XIII) (1 hour at 140°), 2-β-methoxypropenylbenzselenazole, (XIV) (30 minites at 120°). and for the ethylmethylsulfates of 2-β-methylmercaptobutenylbenzthiazole (XVI) and 2-β-methylmercaptostyrylbenzthiazole (XII) (10 minutes at 120°) were as indicated.

Synthesis of the merocyanines . The conditions for preparing the merocyanines, the yields, the melting points of the dyes and the analytical results are set forth in Table 4. The following symbols have been adopted for the initial products in this table: 3-ethylrhodanine – I, 3-ethyl-5-acetanilinomethylenerhodanine – II, iodoethylate of 2-ethylbenzoxazole – IX. iodoethylate of 2-β-anilinopropenyl-benzoxazole – X, ethylperchlorate of 2-β-anilinoisobutenylbenzthiazole – XI. The conventraion sumbols for the quaternary salts of the heterocyclic bases and their derivatives are set forth above in the description of the synthesis(III – VIII and XII – XVI.

In all cases. the dyes which were formed on cooling were filtered off. washed with water and ethyl alcohol, and recrystallized to constant melting point. In certain cases, preliminary chromatography on aluminum oxide in benzene solution was utilized.

SUMMARY

1. A number of dimethinemerocyanine derivatives of 3-ethylrhodanine with various heterocyclic nitrogenous radicals containing the alkyl or phenyl group in the alpha or beta positions of the polymethine chain were synthesized.

2. It was made clear that the introduction of an alkyl or phenyl group into the alpha or beta positions of the polymethine chain of the dimethinemerocyanines with the benzthiazole and benzoxazole radicals causes a bathochromic displacement of the absorption maximum.

3. It was shown that the bathochromic displacement of the absorption maximum caused by the introduction of the methyl group into the alpha position of the external polymethine chain of the merocyanines which were investigated, diminishes with increasing basicity of the nitrogenous heterocyclic radical, and in the case of the dye with a 4-phenylthiazole radical, becomes hypsochromic.

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PREPARATION OF ALIPHATIC-AROMATIC N-BIS-(CHLOROETHYL)-AMINES

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Aliphatic-aromatic N-bis-(chloroethyl)-amines, $[Ar(CH_2)_nN(CH_2CH_2Cl)_2]$ have been comparatively little studied, although they are of undoubted interest for biological research. In the present work, we prepared new compounds of this type, specifically, benzyl-N-bis-(chloroethyl)-amines with alkoxy groups in the aromatic nucleus; in addition, certain other analogous compounds were also synthesized. In the synthesis of benzyl-N-bis-(chloroethyl)-amines, the most convenient method proved to be that [1] in which the starting materials are aromatic chloromethylated compounds of the $(ArCH_2Cl)$ type. The N-bis-(hydroxyethyl)-benzylamines, $[ArCH_2N(CH_2CH_2OH)_2]$, are formed by the action on them of diethanolamine, and the hydroxy groups are replaced by halogen by any method. The success of the synthesis depends, in large measure, on the availability of the initial chloromethylated compound and on its properties.

Almost all of the initial chloromethylated alkoxycompounds were obtained by us by the action of paraform and hydrogen chloride in an anhydrous benzene medium on phenol ethers, and only 4-methoxy-3-nitrobenzylchloride was prepared by the action on o-nitroanisole of formalin and hydrogen chloride in the presence of zinc chloride [2].

In addition, we used other methods, for the most part ones which have already been described in the literature for example: β-chloromethylnaphthalene was prepared by chlorinating β-methylnaphthalene [3], p-cyanobenzylbromide, by the bromination of p-tolunitrile [4], while the o- and m-methoxybenzylchlorides were prepared from the corresponding methoxybenzyl alcohols by replacing the hydroxy group with chlorine [5].

We utilized new data in working out the methods for preparing certain of the starting materials, to wit, m-methoxybenzyl alcohol and m-methyoxybenzoic acid. We prepared m-methoxybenzoic acid by oxidizing m-methoxyacetophenone with sodium hypochlorite; there is no reference to such a method of preparing it in the literature. The conversion of m-methoxybenzoic acid into m-methoxybenzyl alcohol was accomplished previously [6] by electrolytic reduction; we reduced this acid with the aid of lithium aluminum hydride; in addition, we prepared the amide of the acid and reduced it to the methoxybenzyl alcohol by means of a sodium amalgam. Both this and the other method gave completely satisfactory results, but the first of them $(LiAlH_4)$ is more convenient for experimental work.

In the majority of cases, the condensation of all of the chloromethylated compounds obtained was carried out without solvent, and the latter was required only in the condensation of m-methoxybenzylchloride and p-methoxy-m-nitrobenzylchloride. Either benzene or chloroform was used as solvent. The substituted benzyl-bis-(hydroxyethyl)-amines formed as a result of the condensation were not isolated in the pure form, but after the condensation had been carried out, they were at once subjected to the action of thionyl chloride. The benzyl-N-bis-(chloroethyl)-amines thus obtained were isolated either in the form of the bases, or in the form of the hydrochlorides (Table 1).

EXPERIMENTAL

Chloromethylation of the phenol ethers. 1.4 Mole of paraform (well ground and screened through a fine sieve) was required per mole of phenol ether, and anhydrous benzene was required in a 4-fold quantity in relation to the quantity of phenol ether; a stream of hydrogen chloride was passed into the mixture obtained for 4.5 hours at a temperature of 0°. The small colorless precipitate which was left was filtered off, and the benzene solution was treated in the usual way. After distilling off the benzene, the residue was vacuum distilled. The chloromethylated compounds presented in Table 2, were obtained in this manner.

m-Methoxy benzoic acid. 10 g of m-methyoxyacetophenone was gradually added to sodium hypochlorite, prepared by saturating a mixture of 30 g of sodium hydroxide, 40 ml of water and 40 g of ice with chlorine until the weight increase amounted to 21.5 g. As the reaction proceeded, evolution of heat and strong foaming was observed; by external cooling with ice, the temperature was prevented from rising above 80° due to the heat evolution. After adding the m-methoxyacetophenone, the reaction mixture was stirred for 1.5 hours more, and then the solution was filtered off and sodium bisulfite was added to the filtrate in the required quantity. The m-meth-

TABLE 1

Compounds of the structure $ArCH_2N(CH_2CH_2Cl)_2$

Ar	B.p. of the base	M.p. of the hydrochloride	Formula of the hydrochloride	Solvent	Carbon (in %)		Hydrogen (in%)		Nitrogen (in %)		Chlorine (in %)	
					Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$p-CH_3OC_6H_4-$ . . .	150–160° at 5 mm	105-107°	$C_{12}H_{18}ONCl_3$	Benzene	48.24	48.28	6.03	6.23	4.69	4.55	35.67	35.92
$o-CH_3OC_6H_4-$ . . .	154–156° at 3 mm	124-125.5	$C_{12}H_{18}ONCl_3$	Benzene-chloroform mixture	48.24	48.22	6.03	6.26	4.69	4.55	35.67	36.05
$m-CH_3OC_6H_4-$ . . .	159–163° at 2–3 mm	101-103	$C_{12}H_{18}ONCl_3$	Toluene	48.24	48.58	6.03	6.16	4.69	4.75	35.67	35.62
$p-C_2H_5OC_6H_4-$ . .	165–167° at 2–4 mm	120-121.5	$C_{13}H_{20}ONCl_3$	Benzene	50.43	50.24	6.81	6.44	4.51	4.53	34.30	34.07
$p-C_3H_7OC_6H_4-$ . .	165–170° at 2–3 mm	124.5-126.5	$C_{14}H_{22}ONCl_3$	Benzene	51.46	51.96	6.74	6.58	4.28	4.37	32.62	32.08
$p-iso-C_3H_7OC_6H_4-$	167–170° at 3–4 mm	148.5-150.5	$C_{14}H_{22}ONCl_3$	Benzene	51.46	51.58	6.74	6.52	4.28	4.45	32.62	32.59
$p-C_4H_9OC_6H_4-$ . .	178–184° at 2–4 mm	129-130	$C_{15}H_{24}ONCl_3$	Benzene	52.87	53.02	7.04	7.02	4.11	4.33	31.25	31.31
$3,4-(CH_3O)_2C_6H_3$. .	160–170° at 2–3 mm	175-176	$C_{13}H_{20}O_2NCl_3$	Benzene-alcohol mixture	47.48	47.57	6.08	5.93	4.26	4.57	32.42	32.33
$4-CH_3O-3-NO_2C_6H_3-$	–	130-132	$C_{12}H_{17}O_3N_2Cl_3$	Methyl alcohol	41.92	42.24	4.94	5.28	8.15	8.50	–	–
$p-CNC_6H_4-$	–	125.5-127.5	$C_{12}H_{15}N_3Cl_3$	Benzene-alcohol mixture	49.06	49.24	5.11	5.06	9.54	9.44	36.28	35.81
$\beta-C_{10}H_7$	–	161-163	$C_{15}H_{18}NCl_3$	Ethyl acetate-alcohol mixture	56.50	56.69	5.65	5.78	4.39	4.27	33.44	33.12

oxybenzoic acid was isolated by acidifying the solution with hydrochloric acid; after recrystallization from water, the acid melted at 105-106°; the yield was 7 g.

The amide of m-methoxybenzoic acid was prepared from the methyl ester of the acid, prepared by esterification in the presence of sulfuric acid. A mixture of 10 g of the methyl ester of m-methoxybenzoic acid and 25 ml of aqueous ammonia was placed in a thick-walled vessel and saturated, while being cooled, with gaseous ammonia, after which the vessel was tightly covered and the mixture was shaken at room temperature for 30 hours. The amide of the acid which precipitated melted at 132-134° after recrystallization from alcohol; it was insoluble in water, difficultly soluble in benzene and soluble in alcohols.

6.885 mg substance: 0.559 ml N_2 (24°, 727 mm). Found %: N 8.92. $C_8H_9O_2N$. Calculated %: N 9.27.

m-Methoxybenzyl alcohol. a) 5 g of m-methoxybenzoic acid, dissolved in a mixture of 140 ml of dry ether and 100 ml of benzene, was gradually added to 1.88 g lithium aluminum hydrode in 40 ml of dry ether; a vigorous evolution of heat was thereupon observed; after the addition of the m-methyoxybenzoic acid, the stirring and heating were continued for 1 hour and the mixture was then cooled and initially 11-12 ml of water and then a solution of 7.8 ml of sulfuric acid in 156 ml of water was added; the ether-benzene layer was separated, washed with water and dried. After distilling off the solvents, the residue was vacuum distilled; the b.p. was 130-135° at 11-12 mm, and the yield, 3 g.

b) 200 g of 5% sodium amalgam was added in small portions to a mixture of 4 g of the amide of m-methoxybenzoic acid, 30 ml of alcohol and 30 ml of water, with the acidity of the solution being maintained by the addition initially of acetic acid and then of 50% sulfuric acid. Upon completion of the reaction, the mercury was separated, the aqueous layer was neutralized with 20% NaOH solution and the alcohol was driven off in a vacuum, after which the solution was extracted with ether. After distilling off the ether the residue was vacuum distilled. 1.8 g of the methoxybenzyl alcohol with a b.p. of 130° at 20-25 mm was obtained.

m-Methoxybenzyl chloride was prepared by the action of phosphorus trichloride on m-methoxybenzyl alcohol in a chloroform solution; the b.p. was 106-108° at 12-14 mm.

Preparation of substituted benzyl-bis-(chloroethyl)-amines. 0.98 Mole of diethanolamine which was heated to 65° was placed in a flask equipped with a stirrer, a reflux condenser, a thermometer and a dropping funnel. The corresponding chloromethylated compounds ($ArCH_2Cl$) were added in the form of drops at this temperature, and while the mixture was being stirred at such a rate that the temperature within the reaction mixture did not rise above 75-80°; the reaction mass was then heated for 4-5 hours more at a temperature of 95-98°, after which it was cooled to 65° and a benzene solution of thionyl chloride (6 moles) was gradually added, and the solution again heated for 3 hours (temperature in the flask around 80°); the benzene and excess thionyl chloride were then distilled off in a vacuum. The oily substance left was dissolved in water, separated by filtration from resinous admixtures, and a concentrated solution of soda was added to the filtrate until the reaction was alkaline to litmus. The substance which separated was extracted with ether and the ethereal solution was washed with water and dried with sodium sulfate. The ether was driven off and the residue was vacuum distilled. The distilled substance was dissolved in ether and an ethereal solution of hydrogen chloride was gradually added to the solution. The hydrochlorides of the substituted benzyl-N-bis-(chloroethyl)-amines were recrystallized from organic solvents.

TABLE 2

Formula	B. p.	Yield (in %)
p-$CH_3OC_6H_4CH_2Cl$	86-95° (3-5 mm)	50-55
p-$C_2H_5OC_6H_4CH_2Cl$	108-110 (5-6 mm)	45-50
p-$C_3H_7OC_6H_4CH_2Cl$	118-122 (7-9 mm)	50
p-iso-$C_3H_7OC_6H_4CH_2Cl$	112-116 (7-8 mm)	50
p-$C_4H_9OC_6H_4CH_2Cl$	132-133 (3-5 mm)	68-70
3,4-$(OCH_3)_2C_6H_3CH_2Cl$	135-145 (10 mm) m.p. 68-71	38

SUMMARY

Nucleus-substituted benzyl-N-bis-(chloroethyl)-amines which had not previously been described in the literature were prepared and new data relative to the method of preparing certain of the starting materials were submitted.

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4-ALKOXYMETHYL- AND 4-ARYLOXYMETHYL-2-(p-AMINOPHENYL)-THIAZOLES

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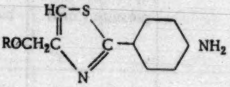
In a preceding work [1] the synthesis of 6-aminobenzthiazoles with alkoxy and aryloxymethyl groups in position 2 was described.

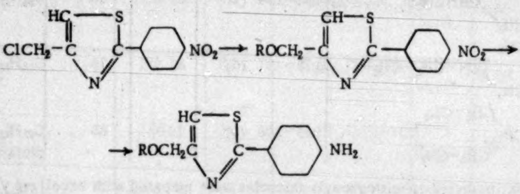
In the present work the synthesis of similar derivatives of thiazole — the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles of the general formula:



are described.

3 Isomeric (p-aminophenyl)-thiazoles [2] are described in the literature but compounds simultaneously containing the p-aminophenyl and alkoxy or aryloxymethyl radical have not been prepared by anyone up to this time.

The synthesis under consideration was accomplished by the reaction of 4-chloromethyl-2-(p-nitrophenyl)-thiazole with alcoholates and phenolates and subsequent reduction of the ethers of 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole into corresponding amino derivatives in accord with the scheme:



where R = CH_3, C_2H_5, C_3H_7(n- and iso-), C_4H_9 (n- and iso-), C_5H_{11} (iso),

C_6H_{11}, C_6H_5, p-ClC_6H_4, o-$CH_3OC_6H_4$, p-$CH_3OC_6H_4$, $C_6H_5CH_2$

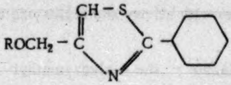
The initial 4-chloromethyl-2-(p-nitrophenyl)-thiazole is well known and was prepared by nitrating 4-chloromethyl-2-phenylthiazole [3]. Preliminary experiments showed that, under the conditions which we used for the synthesis of 2-alkoxymethyl-6-nitrobenzthiazoles [1], only sodium methylate and benzylate react with 4-chloromethyl-2-(p-nitrophenyl)-thiazoles with the formation of 4-methoxymethyl- and 4-benzyloxymethyl-2-(p-nitrophenyl)-thiazoles. The action of other alcoholates leads to the formation of high-melting products which were not investigated in greater detail.

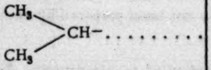
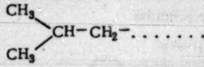
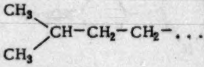
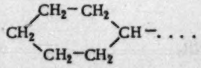
Another method was selected which consisted in initially obtaining the 4-alkoxymethyl-2-phenylthiazoles, which were then nitrated. The 4-alkoxymethyl-2-phenylthiazoles were prepared in excellent yields by heating 4-chloromethyl-2-phenyl thiazole with the corresponding alcoholates. They consisted of colorless liquids which formed picrates which crystallized well. The boiling points, yields and analytical results for the 4-alkoxymethyl-2-phenylthiazoles are given in Table 1. All the preparations set forth are new compounds.

By the nitration of 4-alkoxymethyl-2-phenylthiazoles, products were formed, in the molecule of which the nitro group occupies, as one would naturally expect, the para position in the phenyl ring, which was demonstrated by oxidation to p-nitrobenzoic acid. As in the case of nitration of the 2-alkoxymethylbenzthiazoles, we did not succeed in obtaining the normal nitration products under the conditions which we used (sulfuric acid medium), when the alkyl group was branched. 4-Isobutoxymethyl-2-phenylthiazole, which formed 4-isobutoxymethyl-2-(p-nitrophenyl)-thiazole in a 25% yield, was an exception. The nitration of 4-isopropoxymethyl-2-phenylthiazole led to the formation of a product with a m.p. of 80°, which contained 4% more nitrogen and sulfur than were required. We did not investigate this product in more detail. By nitrating 4-isoamyloxymethyl-2-phenylthiazole, a product with a m.p. of 167-168°, which agreed in its nitrogen and sulfur content with the dealkylation product — 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole, was isolated.

TABLE 1

4-Alkoxymethyl-2-phenylthiazoles of the General Formula:



Sequence No. of the compound	R	B.p. at the given pressure (mm)	Yield (in %)	M.p. of the picrate	Empirical formula	Analytical results	
						Nitrogen (in %)	
						Found	Calculated
I	C_2H_5–.	172–174° (12)	82	–	$C_{12}H_{13}ONS$*	6.07 6.16	6.39
II	$CH_3-CH_2-CH_2$–.	183–185 (12)	71	–	$C_{13}H_{15}ONS$	5.75 5.69	6.00
III		165–167 (5)	72	109°	$C_{19}H_{18}O_8N_4S$ (picrate)	12.12 12.34	12.12
IV	$CH_3-CH_2-CH_2-CH_2$–. . .	173–174 (5)	80	–	$C_{14}H_{17}ONS$	5.19 5.24	5.67
V		183–184 (10)	82	85	$C_{14}H_{17}ONS$	5.28 5.11	5.67
VI		179–181 (5)	81	76	$C_{15}H_{19}ONS$	5.13 5.14	5.36
VII		206–208 (5)	70	89	$C_{22}H_{22}O_8N_4S$ picrate	11.39 11.41	11.15

The 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were prepared with excellent yields by heating 4-chloromethyl-2-(p-nitrophenyl)-thiazole with the corresponding phenols in acetone solution in the presence of anhydrous potash. The preparations of this groups which we obtained are set forth in Table 2. They consisted of substances which crystallized very well. The 4-alkoxymethyl-2-(p-nitrophenyl)-thiazoles were quite soluble in alcohol, and ether, and were poorly soluble in water. They were recrystallized from alcohol. The 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were poorly soluble in alcohol; they were therefore recrystallized from glacial acetic acid

The 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were reduced in an alcohol-water medium by iron filings in the presence of acetic acid. The majority of the amines obtained were isolated in the pure form, and the rest were identified in the form of the hydrochlorides and acetyl derivatives. The amines which were isolated consisted of colorless needles, quite soluble in alcohol and poorly soluble in water. They were recrystallized from aqueous alcohol. The yields, melting points and analytical data for the amines isolated are set forth in Table 3. We did not succeed in isolating the product of the reduction of 4-benzyloxymethyl-2-(p-nitrophenyl)-thiazole, probably as a consequence of the low stability of the benzyloxy group.

The hydrochlorides of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles consisted of yellow colored needles. The hydrochlorides of the alkoxymethyl-derivatives were quite soluble in water, but hydrolyzed at the same time. The salts were readily diazotized and yielded azo dyes by combination with β-naphthol. The hydrochlorides of 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were difficultly soluble even in boiling water. They were recrystallized from alcohol The melting points and analytical data of the hydrochlorides are set forth in Table 4.

The acetyl derivatives of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were readily obtained in the crystalline form; they were recrystallized from benzene. The diacetyl derivatives were recrystallized from glacial acetic acid.

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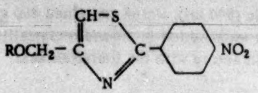
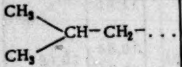
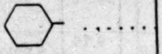
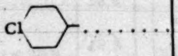
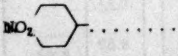
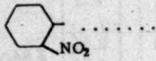
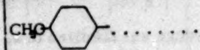
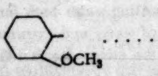
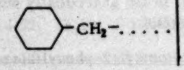
* Found %: S 14.50, 14.68. Calculated %: S 14.60

TABLE 2

4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-nitrophenyl)-thiazoles of the General Formula:



Sequence No. of the compound	R	M.p.	Yield (in %)	Empirical formula	Analytical results			
					Nitrogen (in %)		Sulfur (in %)	
					Found	Calculated	Found	Calculated
I	CH_3-	143–144*	80	$C_{11}H_{10}O_3N_2S$	11.23 11.04	11.20	12.67 12.77	12.80
II	CH_3-CH_2-	90–90.5	75	$C_{12}H_{12}O_3N_2S$	10.46 10.57	10.60	12.05 12.15	12.12
III	$CH_3-CH_2-CH_2-$	84–84.5	55	$C_{13}H_{14}O_3N_2S$	10.17 10.24	10.07	11.43 11.60	11.51
IV	$CH_3-CH_2-CH_2-CH_2-$	62	50	$C_{14}H_{16}O_3N_2S$	9.80 9.85	9.58	11.02 11.08	10.96
V	 $(CH_3)_2CH-CH_2-$ . . .	49.5–50	25	$C_{14}H_{16}O_3N_2S$	9.59 9.71	9.58	11.05 11.15	10.95
VI		112	70	$C_{16}H_{12}O_3N_2S$	9.01 9.02	8.97	10.17 10.36	10.25
VII		120	80	$C_{16}H_{11}O_3N_2SCl$	8.05 8.20	8.08	10.34 10.41	10.24*
VIII		198	31	$C_{16}H_{11}O_5N_3S$	11.70 11.82	11.76	8.86 9.02	8.96
IX		216–217	15	$C_{16}H_{11}O_5N_3S$	11.51 11.50	11.76	8.88 8.80	8.96
X		152	70	$C_{17}H_{14}O_4N_2S$	8.13 8.31	8.18	9.29 9.40	9.35
XI		109.5–110	64	$C_{17}H_{14}O_4N_2S$	7.98 8.11	8.17	9.36 9.37	9.35
XII		147	60	$C_{17}H_{14}O_3N_2S$	8.81 8.85	8.59	10.06	9.81

The 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-acetylaminophenyl)-thiazoles consisted of colorless crystals with a melting point above 100°. The melting points and analytical data are presented in Table 5.

EXPERIMENTAL

4-Chloromethyl-2-phenylthiazole was prepared by condensing symmetrical dichloroacetone and thiobenzamide under the conditions described in the literature [3].

4-Chloromethyl-2-(p-nitrophenyl)-thiazole was also prepared in accordance with the literature data [4], with small changes. 27 g of 4-chloromethyl-2-phenylthiazole was added in portions to 50 ml of concentrated sulfuric acid while it was being mechanically stirred. The solution obtained was cooled to +5°, and a mixture of 30 ml of nitric acid (d 1.5) in 3) ml of concentrated sulfuric acid was added in the form of drops at this temperature over a period of 30-40 minutes. The reaction mass was stirred at room temperature for 1 hour and then was poured out in a fine stream into a 20% solution of sodium hydroxide (800 ml), which contained 800 g of crushed ice. The precipitate which settled out was filtered off, washed with water, dried in air and recrystallized from alcohol. The yield was 22.5 g (70%). The m.p. was 120°, which was in accord with the literature data.

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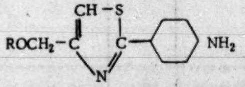
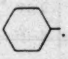
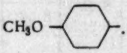
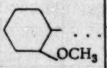
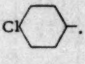
* It was analyzed for chlorine content.

TABLE 3

4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-aminophenyl)-thiazoles of the General Formula :



Sequence No. of the compound	R	M.p.	Yield (in %)	Empirical formula	Analytical results			
					Nitrogen (in %)		Sulfur (in %)	
					Found	Calculated	Found	Calculated
I	CH_3-	77°	65	$C_{11}H_{12}ON_2S$	12.37 12.46	12.12	14.25	14.54
II	$CH_3-CH_2-CH_2-$	75	41	$C_{13}H_{16}ON_2S$	11.45 11.41	11.29	12.94 13.04	12.90
III	$(CH_3)_2CH-CH_2-$	85	80	$C_{14}H_{18}ON_2S$	10.84 10.71	10.68	11.97 12.00	12.21
IV		98	75	$C_{16}H_{14}ON_2S$	9.70 9.81	9.92	11.05 10.89	11.34
V		144-145	80	$C_{17}H_{16}O_2N_2S$	8.91 9.11	8.98	10.23 10.35	10.25
VI		130-131	60	$C_{17}H_{16}O_2N_2S$	8.83 9.11	8.98	10.26 10.37	10.25
							Chlorine (in %)	
VII		119	63	$C_{16}H_{13}ON_2SCl$	8.91 8.74	8.84	11.11 10.94	11.21

4-Alkoxymethyl-2-phenylthiazoles (I-VII, Table 1). 1). 0.7 g of sodium was dissolved in 20 ml of the appropriate anhydrous alcohol, and a solution of 6.2 g of 4-chloromethyl-2-phenylthiazole in 15 ml of the same alcohol was added to the solution obtained. The mixture was heated on a boiling water bath for 3 hours and the alcohol was then driven off in a vacuum, the residue was stirred into 20 ml of water and extracted with ether. The ethereal solution was dried with roasted sodium sulfate and, after driving off the ether, the residue was vacuum distilled. We did not succeed in obtaining a few of the compounds (V, VI) in the analytically pure form. The picrates were obtained in an alcoholic solution and recrystallized from alcohol .

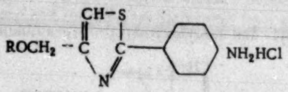
Nitration of-4-ethoxymethyl-2-phenylthiazole. 6.6 g of 4-ethoxymethyl-2-phenylthiazole was added to 15 ml of concentrated sulfuric acid which was being cooled and mechanically stirred, and the solution obtained was cooled to -1 to -2°. At this temperature, a mixture of 7 ml of nitric acid (d 1.5) in 10 ml of concentrated sulfuric acid was added in the form of drops over a period of 30 minutes. The reaction mixture was stirred for 30 minutes more and then poured out into a 20% solution of sodium hydroxide (160 ml), containing 300 g of crushed ice. The precipitate which settled out was filtered off, washed, dried in air, and recrystallized from alcohol. The yield of recrystallized product was 6 g (75%). The m.p. was 90°.

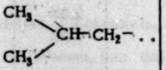
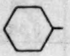
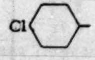
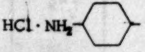
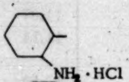
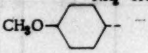
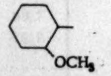
Preparations III, IV and V (Table 2) were prepared analogously.

4-Methoxymethyl-2-(p-nitrophenyl)-thiazole (I) and 4-benzyloxymethyl-2-(p-nitrophenyl)-thiazole (XII) were prepared by the reaction of 4-chloromethyl-2-(p-nitrophenyl)-thiazole with sodium methylate and sodium benzylate analogously to the 4-alkoxymethyl-2-phenylthiazoles.

TABLE 4

Hydrochlorides of 4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-aminophenyl)-thiazoles of the General Formula:



Sequence No. of the compound	R	M.p.	Empirical formula	Analytical results	
				Nitrogen (in %)	
				Found	Calculated
I	CH_3-	185–186° (with decomp.)	$C_{11}H_{13}ON_2SCl$	9.77 9.69	10.87
II	CH_3-CH_2-.	Hygroscopic	–	–	–
III	$CH_3-CH_2-CH_2-$. .	181–182 (with decomp.)	$C_{13}H_{17}ON_2SCl$	9.89 9.96	9.84
IV	$CH_3-CH_2-CH_2-CH_2$	185–187 (with decomp.)	$C_{14}H_{19}ON_2SCl$	9.10 9.13	9.88
V	 $\overset{CH_3}{\underset{CH_3}{>}}CH-CH_2-$ . .	187 (with decomp.)	$C_{14}H_{19}ON_2SCl$	9.54 9.37	9.38
VI		186–187	$C_{16}H_{15}ON_2SCl$	8.75 8.84	8.78
VII		215–216 (with decomp.)	$C_{16}H_{14}ON_2SCl_2$	7.85 8.01	7.98
VIII		230–235 (with decomp.)	$C_{16}H_{17}ON_3SCl_2$	11.07 10.94	11.35
IX		222–223 (with decomp.)	$C_{16}H_{17}ON_3SCl_2$	11.30	11.35
X		197 (with decomp.)	$C_{17}H_{17}O_2N_2SCl$	7.78 7.68	8.03
XI		180 (with decomp.)	$C_{17}H_{17}O_2N_2SCl$	7.97 7.79	8.03

A product with a m.p. of 80° was obtained by nitrating 4-isopropoxymethyl-2-phenylthiazole. Analysis of this product showed an increased nitrogen and sulfur content.

Found %: N 14.32; 14.14; S 16.44; 4-Isopropoxy-2-(p-nitrophenyl)-thiazole. Calculated %: N 10.07; S 11.51.

We have still not elucidated of what the product isolated consists.

The nitration of 4-isoamyloxy-2-phenylthiazole under the same conditions led to the formation of a product with a m.p. of 169-170°, which, agreed in its analytical data with those of 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole.

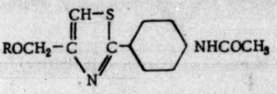
Found %: N 11.66; 11.84; S 13.46. $C_{10}H_8O_3N_2S$. Calculated %: N 11.76; S 13.44.

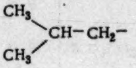
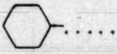
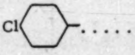
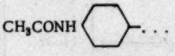
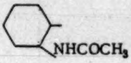
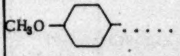
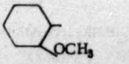
We did not succeed in isolating the product of the nitration of 4-cyclohexyloxymethyl-2-phenylthiazole.

Position of the nitrogroup in the nitration products of the 4-alkoxymethyl-2-phenylthiazoles. 0.5 g of the nitrophenylthiazole derivative was added to a solution of 5 g of potassium bichromate in a mixture of 20 ml of concentrated sulfuric acid and 15 ml of water, and the mixture was boiled moderately for 1 hour. After cooling, 50 ml of water was added and the white precipitate which settled oout was filtered off, washed with water and dried. The m.p. was 238°; the substance displayed no melting point depression in a mixed sample with p-nitrobenzoic acid. The yield of p-nitrobenzoic acid amounted on the average to around 70%.

TABLE 5

Acetyl Derivatives of 4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-aminophenyl)-thiazoles of the General Formula:



Sequence number of the compound	R	M.p.	Empirical formula	Analytical results	
				Nitrogen (in %)	
				Found	Calculated
I	CH_3—.	121°	$C_{13}H_{14}O_2N_2S$	10.58 10.63	10.67
II	CH_3-CH_2—. . . .	150	$C_{14}H_{16}O_2N_2S$	10.07 9.90	10.14
III	$CH_3-CH_2-CH_2$—	146—147	$C_{15}H_{18}O_2N_2S$	9.70 9.69	9.65
IV	$CH_3-CH_2-CH_2-CH_2$—	101—102	$C_{16}H_{20}O_2N_2S$	9.39 9.22	9.21
V		109—110	$C_{16}H_{20}O_2N_2S$	9.23 9.03	9.21
VI		141—142	$C_{18}H_{16}O_2N_2S$	8.54 8.72	8.64
VII		171	$C_{18}H_{15}O_2N_2SCl$	7.79 7.69	7.81
VIII		259	$C_{20}H_{19}O_3N_3S$	11.07 11.11	11.02
IX		217	$C_{20}H_{19}O_3N_3S$	10.50	11.02
X		170—171	$C_{19}H_{18}O_3N_2S$	7.80 7.97	7.90
XI		161—161.5	$C_{19}H_{18}O_3N_2S$	7.64 7.61	7.90

4-Aryloxymethyl-2-(p-nitrophenyl)-thiazoles. A mixture, consisting of 2.5 g (0.01 mole) of 4-chloromethyl-2-phenylthiazole, 0.02 mole of the corresponding phenol, 2.7 g (0.02 mole) of anhydrous potash and 75 ml of dry acetone, was boiled on a water bath for 24-25 hours. After distilling off the acetone, the residue was stirred into water, filtered, washed with a 5% solution of sodium hydroxide, then with water, and after drying, was recrystallized from glacial acetic acid. The data for the preparations obtained are set forth in Table 2 (VI-XII).

Reduction of 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles. 10 ml of 20% acetic acid was added to a solution or a suspension of 0.01 mole of the nitrophenyl derivative of thiazole in 50 ml of alcohol; the reduction was carried out with iron filings, just as in the reduction of the 2-alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles. The amines isolated in the crystalline form are presented in Table 3. They consisted of colorless crystals. Alcoholic and ethereal solutions fluoresced with a beautiful violet color. The liquid amines were extracted with ether, the ethereal solution was washed with sodium bicarbonate and dried with anhydrous sodium sulfate. After distilling off the ether, the residue was identified in the form of the hydrochloride and the acetyl derivative.

The hydrochlorides of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were prepared by mixing an alcoholic solution of the amine with an ethereal solution of hydrogen chloride. The precipitate of the salt which settled out was recrystallized from alcohol.

The acetyl derivatives were prepared by briefly boiling the amine with acetic anhydride. The monoacetyl derivatives were recrystallized from benzene and the diacetyl derivatives from glacial acetic acid.

SUMMARY

1. A number of 4-alkoxymethyl-2-phenylthiazoles were prepared; the corresponding p-nitrophenyl derivatives were obtained by nitrating them.

2. The corresponding aryloxy derivatives were prepared from 4-chloromethyl-2-(p-nitrophenyl)-thiazole by reaction with phenols.

3. The corresponding amines were prepared by reducing the 4-alkoxymethyl-and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles.

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SYNTHESES BASED ON ANABASINE

VII. SULFONATION OF ANABASINE BY PYRIDINESULFOTRIOXIDE

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Our preceding work [1] was devoted to the study of the amination of anabasine, N-methylanabasine and nicotine by sodium amide in the absence of solvents. In the present article, the results of the sulfonation of anabasine, piperidine and certain of their derivatives by pyridinesulfotrioxide are reported.

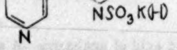
It is well known from the literature data that pyridinesulfotrioxide [2,4] is used for preparing sulfonic acids with the sulfo group located on a carbon atom, and of the so-called sulfamic acids (with the sulfo group at the nitrogen atom) [4-7].

We used this reagent to sulfonate anabasine with the object of synthesizing a sulfamic acid based on the imine group of the piperidine ring. The reaction was conducted under the conditions for sulfonating piperidine [8,9] – at 0° in an aqueous medium in the presence of potash The sulfamic acid of anabasine was isolated in the form of the potassium salt with a yield of 51.1%. The potassium salt, after recrystallization from alcohol, consisted of colorless crystals with a m.p. of 212-213° and, according to the analysis, contained one sulfo group.

By mixing alcoholic solutions of the potassium salt and picric acid, a picrate was obtained which was identical with anabasine picrate. The dry distillation of a mixture of the potassium salt of the sulfamic acid of anabasine with potassium cyanide yielded anabasine. This indicated the great lability and ready cleavability of the sulfo group.

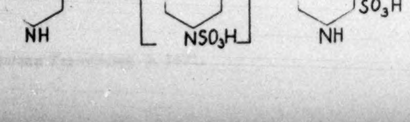
An attempt was made to isolate the sulfamic acid from the potassium salt via heating it with an equimolecular quantity of hydrogen chloride (in alcohol). An oil was thereby obtained, which, in contrast to anabasine, did not dissolve in acetone. It did not crystallize during prolonged standing in a desiccator. We succeeded in recovering the potassium salt from the oil, but in an insignificant yield (12%). Evidently, it was not an individual product, but consisted of a mixture of the sulfamic acid and anabasine sulfate. This permits us to conclude that the sulfamic acid of anabasine is unstable in the free form.

The potassium salt was completely hydrolyzed by a brief heating with 2% hydrochloric acid solution in the presence of barium chloride, and a precipitate of barium sulfate settled out at the same time. Sulfamic acids behave in this way during hydrolysis [5-8]. This gives us the right to assume that the sulfamic acid obtained, which was characterized in the form of the potassium salt, was the sulfamic acid of anabasine:



This is all the more probable since N-methyl- and N-acetylanabasine do not yield the corresponding acids with pyridinesulfotrioxide under similar conditions.

It is of interest to note that, under analogous conditions, Rubtsov, completely unexpectedly, as the author reports, succeeded in obtaining 2-piperidinesulfonic acid from piperidine [8]. Our attempt to obtain the corresponding acids from N-methyl- and N-acetylpiperidine gave negative results. This fact indicates that, in the sulfonation of piperidine, sulfamic acid is apparently formed initially, and then isomerizes into 2-piperidinesulfonic acid:



Paal and Hubaleck indicate that sulfamic acid is readily hydrolyzed, and the authors consider that, even when the salt of the sulfamic acid of piperidine is stored, partial isomerization occurs. We did not observe such properties in the salt of the sulfamic acid of anabasine.

The experiments which were carried out show that the nitrogen of the piperidine ring of anabasine more strongly retains a sulfo group near it. The pyridine ring in anabasine definitely influences this.

Sulfonation of anabasine with pyridinesulfotrioxide at room temperature permitted the sulfamic acid to be obtained in a considerably smaller yield (15%), while when the reaction was carried out by heating the mixture at 100°, the acid was not obtained at all.

The reaction of anabasine with pyridinesulfotrioxide involving the direct reaction of these compounds was also studied. Experiments involving heating mixtures of the reagents, taken in various molar ratios, at 100 and 150° for 10-15 hours, did not permit us to isolate the crystalline products in appreciable quantities. The reaction was not carried out above 150°, since it is known from the literature data that at 200°, pyridinesulfotrioxide is itself isomerized into the β-sulfonic acid of pyridine [11].

EXPERIMENTAL

We prepared pyridinesulfotrioxide by the method of Terentyev [6].

Sulfonation of anabasine with pyridinesulfotrioxide at 0°. 40 g of ice and 5 g of pyridinesulfotrioxide were added to a solution of 5 g of anabasine in 25 ml of water. The mixture was stirred for 20 minutes. 4.2 g of potash in 6 ml of water was then added to the mixture and the stirring was continued for 35 minutes while the mixture was cooled with ice water. After this, the solution was concentrated to dryness on a water bath. The residue was treated with anhydrous alcohol while being heated. After distilling off the alcohol, 4.4 g (51.1%) of the potassium salt of the sulfamic acid of anabasine was obtained, which had a m.p. of 212-213° after recrystallization from alcohol.

0.09683, 0.10148 g substance: 0.03171, 0.03083 g K_2SO_4. Found %: K 14.49, 13.48. $C_{10}H_{13}N_2SO_3K$. Calculated %: K 13.93.

Picrate. Upon stirring alcoholic solutions of the potassium salt of the sulfamic acid of anabasine and picric acid, the picrate with a m.p. of 196-197° precipitated. A mixed sample with anabasine picrate melted at 197-198°.

Isolation of the sulfamic acid of anabasine from the potassium salt. An equimolecular quantity of an alcoholic solution of hydrogen chloride (0.065 g) was added to 0.5 g of the potassium salt in anhydrous alcohol. The precipitate of potassium chloride which settled out upon negligible heating was separated and the filtrate concentrated. The residue consisted of an oil which was insoluble in acetone. The oil did not crystallize upon prolonged standing in a desiccator. It yielded a picrate with a m.p. of 198-200° with picric acid. A mixed sample with anabasine picrate melted at 197-200°. Excess 50% potash solution was added to 0.85 g of the oil. The solution was concentrated to dryness. The residue was extracted with anhydrous alcohol. 0.12 g (12%) of the potassium salt with a m.p. of 209-210° was obtained. A mixed sample with the potassium salt of the sulfamic acid of anabasine melted at 209-211°.

Hydrolysis of the potassium salt of the sulfamic acid of anabasine. A small quantity of barium chloride was added to a solution of 0.1702 g of the potassium salt of the sulfamic acid of anabasine in 2% hydrochloric acid. A precipitate of barium sulfate settled out upon negligible heating. A picrate with a m.p. of 196-197° was obtained from the aqueous solution after separating the barium sulfate. A mixed sample with anabasine picrate melted at 196-198°.

SUMMARY

1. The study of the sulfonating action of pyridinesulfotrioxide under various conditions showed that the sulfamic acid can be prepared from anabasine with the aid of this substance.

2. N-Methyl- and N-acetylanabasine, and also the corresponding derivatives of piperidine do not react with pyridinesulfotrioxide under the conditions which permit the preparation of 2-piperidinesulfonic acid.

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AN ALKALOID FROM GLEDITSCHIA TRIACANTHOS L.

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Gleditschia triacanthos L. (fam. Caesalpiniaceae) [the honey locust], is a tree with sharp branched thorns, pinnate leaves and fine greenish-white flowers. It is cultivated in the Caucasus, in Central Asia and in the Crimea for decorative purposes [1].

The leaves and fruit of the honey locust contain 100-400 mg% of ascorbic acid [2], and in the pods are found saponins [3], glucosides [4] and the flavonoid pigments acrammerin [5] and olmelin [6,7].

In 1947-1948 one of the authors of this article (M. V. Tsarev) established that the leaves and flowers of the honey locust contain a considerable quantity of alkaloids and that smaller quantities of alkaloids are found in the thorns, bark and seeds. The young, just-opened leaves are richest in alkaloids — to 1% of the air-dry weight. As the leaf grows, the alkaloid content sharply falls; leaves collected in July contain only traces of alkaloids. The flowers of the honey locust contain 0.3%, and the seeds 0.05% of alkaloids.

A crystalline alkaloid with a m.p. of 227-228°, named triacanthine, was isolated in 1949 from the young leaves of the honey locust.

Our investigations have established that the composition of triacanthine corresponds with the formula $C_8H_{10}N_4$.

Triacanthine crystallizes from alcohol in the form of white rhombic crystals. It is quite soluble in alcohol, more difficultly soluble in chloroform and almost insoluble in water and ether.

Triacanthine is a strong base and is precipitated out from solutions of its salts by strong alkalis. It reduces potassium permanganate at any pH value and is readily oxidized by bromine and chromic acid. Triacanthine forms well crystallized salts with mineral and organic acids: the hydrochloride has a m.p. of 218-219°, the nitrate, a m.p. of 164-166°, the hydrobromide, a m.p. of 215-216°, the picrate, a m.p. of 239-241°, the picrolonate, a m.p. of 229-231° and the sulfates, m.p. of 175-176° and 216-217°. The hydrochloride, the hydrobromide, the nitrate and the sulfates are quite soluble in water and alcohol; the picrate and the picrolonate are insoluble in water and difficultly soluble in alcohol. The iodomethylate of triacanthine consists of white flakes or needles which melt at a temperature of 199-203°. The iodomethylate is insoluble in water, dissolves readily in methyl alcohol and more poorly in ethyl alcohol.

The composition and properties of triacanthine and the melting points of its salts and of the iodomethylate provide a basis for assuming that it is a new alkaloid which has not previously been described in the literature.

EXPERIMENTAL

1. Isolation and Purification of the Alkaloid

Pulverized air-dry leaves of the honey locust were moistened with 10% aqueous ammonia solution and exhaustively extracted with dichloroethane. The extract obtained was treated several times with 5% sulfuric acid until the alkaloids were completely extracted, after which the sulfuric acid solution of triacanthine was rendered alkaline with 50% sodium hydroxide solution and the precipitate which fell out of triacanthine base was filtered off. The triacanthine which was left in the solution was extracted with xhloroform, the chloroform solution was dried with anhydrous sodium sulfate, filtered off, (and the solvent driven off and the solution concentrated to dryness on a water bath.

The triacanthine isolated was dissolved in 5% sulfuric acid, the sulfuric acid solution was rendered alkaline with 50% sodium hydroxide solution, and the alkaloid extracted with chloroform. After drying the solution, the chloroform was driven off, and the triacanthine twice recrystallized from alcohol. 100 g of pure triacanthine which melted at 227-228° was obtained from 20 kg of leaves.

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* Deceased

The triacanthine was subjected to further purification for conducting the elementary analysis for carbon, hydrogen and nitrogen by the methods of Liebig and Dumas. Sulfuric acid (d 1.84) was added in the form of drops to a solution of 0.5 g of triacanthine in 5 ml of alcohol until the reaction was acid to litmus. The sulfate which precipitated was filtered off, recrystallized from alcohol, dissolved in 5 ml of water, rendered alkaline with 30% sodium hydroxide solution, and isolated in the form of triacanthine base by two-fold recrystallization from alcohol. After drying in a vacuum-pistol at 100° for 14 hours, the triacanthine melted at 228°.

4.760 mg substance: 10.336 mg CO_2; 2.683 mg H_2O. 3.860 mg substance: 8.389 mg CO_2; 2.178 mg H_2O. 3.120 mg substance: 0.960 ml N_2 (22°, 735 mm). 3.550 mg substance: 1.092 ml N_2 (22°, 735 mm). Found %: C 59.26, 59.31; H 6.30, 6.31; N 34.46, 34.73. $C_8H_{10}N_4$. Calculated %: C 59.23; H 6.21; N 34.54.

0.0106 g substance; 0.2304 g camphor: Δt 12°. 0.0188 g substance; 0.2528 g camphor: Δt 11°. Found: M 153.36, 169.63. $C_8H_{10}N_4$. Calculated: M 162.19.

The triacanthine picrate, prepared by stirring alcoholic solutions of triacanthine-base and picric acid together, and recrystallization from alcohol, melted at 239-241°.

4.560 mg substance: 7.448 mg CO_2; 1.521 mg H_2O. 2.078 mg substance: 3.68 mg 0.01 N H_2SO_4. 4.812 mg substance: 8.48 mg 0.01 N H_2SO_4. Found %: C 44.57; H 3.73; N 24.80. 24.67. $C_8H_{10}N_4 \cdot C_6H_3O_7N_3$. Calculated %: C 42.97; H 3.35; N 25.06

0.0106 g substance: 0.2502 g camphor: Δt 4.5°. Found: M 376.53. $C_8H_{10}N_4 \cdot C_6H_3O_7N_3$. Calculated: M 391.30.

2. Preparation of the Derivatives

a) A solution of 0.2 g of triacanthine in 5 ml of alcohol was saturated with dry hydrogen chloride. The hydrochloride precipitated in the form of fine white needles, and, after recrystallization from alcohol, melted at 218-219°.

b) Hydrobromic acid (d 1.51) was added in the form of drops to a solution of 0.2 g of triacanthine in 5 ml of alcohol until a precipitate began to appear. After recrystallization from alcohol, the triacanthine hydrobromide had the form of flat white needles which melted at 215-216°.

c) Upon adding nitric acid (d 1.39) in the form of drops to an alcoholic solution of triacanthine, and subsequent cooling for an hour at 0°, lamellar crystals of triacanthine nitrate precipitated. After recrystallization from alcohol, the nitrate had a m.p. of 164-166 and was hygroscopic.

d) The picrolonate of triacanthine was prepared by stirring a solution of 0.2 g of triacanthine in 5 ml of alcohol with 5 ml of an alcoholic solution of picrolonic acid. It crystallized from alcohol in the form of very fine yellow crystals, m.p. 229-231°.

e) The crystalline sulfates, with m.p. 175-176° and 216-217°, were prepared by adding various quantities of sulfuric acid (d 1.84) to an alcoholic solution of triacanthine.

f) 2 ml of methyl iodide was added to a solution of 0.1 g of triacanthine in 5 ml of methyl alcohol and the mixture was heated with a reflux condenser on a water bath for 3 hours, after which the iodomethylate was filtered off and recrystallized from alcohol three times. The m.p. was 199-203°.

The chemical study of triacanthine is being continued.

SUMMARY

1. The new alkaloid triacanthine, with composition $C_8H_{10}N_4$, was isolated from the leaves of Gleditschia triacanthos L. . [The honey locust]

2. The following derivatives of triacanthine were prepared and characterized: the hydrochloride, hydrobromide, nitrate, picrate, picrolonate, the sulfates and the iodomethylate.

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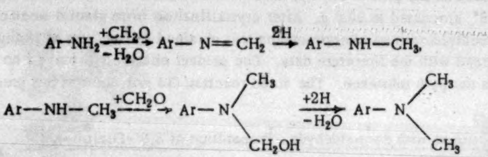
** Consultant's Bureau Translation; p. 589.

THE DIMETHYLATION OF PRIMARY AROMATIC AMINES WITH THE AID OF FORMALDEHYDE. PREPARATION OF 4-NITRODIMETHYLANILINE

B. M. Bogoslovsky

The possibility of methylating amines via their reaction with a mixture of formaldehyde and formic acid, which can be considered as a special case of the widely known Leuckart reaction, has been repeatedly mentioned in the literature. At the same time, however, it must be emphasized that in the overwhelming majority of cases the indicated method of methylation was used only in relation to primary amines and also to α- and β-amino acids of the aliphatic series. It has been applied more rarely to amines of the alicyclic series and still more rarely to heterocyclic amines. One of the few examples of the application of the reaction under consideration to amines of the aromatic series is the conversion of 2,4,6-tribromoaniline into 2,4,6-tribromodimethylaniline [1,2].

The mechanism of the case of methylation of aromatic amines under consideration does not appear to have been studied in detail. In all probability, the process occurs in stages; the monomethyl derivatives are initially formed [3], and these are then converted into the dimethyl derivatives by the following probable scheme:



In both cases, the reducing agent is formic acid, the reducing capacity of which has been repeatedly referred to by many authors.

The comparatively limited application of the possibility of dimethylating primary aromatic amines, evidently, can be explained by their tendency to form the corresponding diarylmethane derivatives by reaction with formaldehyde. The latter direction of the reaction can prove to be competitive, while it sometimes prevails in the case of the conversion under consideration. Thus, in particular, in the case of the methylation of α-amino-pyridine, described by Chichababin and Knunyants, tetramethyl derivatives of diaminodipyridylmethane [4] are finally formed. According to the investigation of Titov and Baryshnikova, this reaction proceeds in stages, to wit: dimethylaminopyridine is formed first and then dimethylaminopyridylcarbinol is formed which, condensing with a second molecule of dimethylaminopyridine, forms the end product–the corresponding dipyridylmethane derivative [5].

If one considers what has been set forth above, it becomes clear that dimethylation in accord with the Leuckart method can have a chance of success only for those aromatic amines in the molecule of which some substituent that inhibits the formation of the diarylmethane derivative is found in the para position to the amino group. Thus, of the three isomeric nitroanilines, only 4-nitroaniline fulfills the set condition; consequently, only when this latter compound is used can the formation of the dimethylated derivative in good yields be expected. It should be noted, incidentally, that the methods for preparing 4-nitrodimethylaniline described in the literature are characterized by comparatively low yields and are often accompanied by the necessity of separating the mixture of amines which is formed; 2- and 3-nitroanilines, with the para position to the amino group unsubstituted, can also form the corresponding diphenylmethane derivatives.

The experiments confirmed the assumptions made above. Actually, 4-nitroaniline was successfully converted into 4-nitrodimethylaniline in very excellant yields. 3-Nitroaniline was converted into 2,2'-dinitro-4,4'-bis-(dimethylamino)-diphenylmethane in equally good yields, while for the case of 2-nitroaniline, we succeeded in making secure the preparation of the corresponding diaminodinitrodiphenylmethane, which evidently underwent further methylation with great difficulty under the conditions which we employed.

EXPERIMENTAL *

1. Reaction of 4-Nitroaniline with Formaldehyde. Preparation of 4-Nitrodimethylaniline

20 g of 4-nitroaniline was dissolved by heating in 45 ml of 100% HCOOH, after which 45 ml of a 30% solution of formaldehyde together with 5 g of paraformaldehyde was added to the transparent solution which was formed. After heating for 30 minutes on a water bath, which was accompanied by the evolution of gas bubbles from the reaction mass, the contents of the flask with the abundant yellow precipitate which was formed, were cooled, the liquid was drawn off, and the precipitate washed with water and dried. The yield of product with a m.p. of 148° amounted to 20 g. After crystallization from glacial acetic acid, 16 g (67%) of 4-nitrodimethylaniline was obtained in the form of bright yellow crystals with a m.p. of 161-163°. A mixed sample with the pure product, prepared by oxidizing 4-nitrosodimethylaniline and which had a m.p. of 162-163°, displayed no melting point depression.

2. Reaction of 3-Nitroaniline with Formaldehyde. Preparation of 2,2'-Dinitro-4,4'-tetramethyldiaminodiphenylmethane

45 ml of a 30% formaldehyde solution with 5 g of paraformaldehyde was added to a heated solution of 20 g of 3-nitroaniline in 45 ml of 100% HCOOH, after which the mixture was heated for 2.5 hours on a water bath. The reaction product which was isolated in the precipitate was filtered off, washed with water and dried. The yield of product which had a m.p. of 188°, amounted to 20.2 g. After crystallization from glacial acetic acid, 17 g (about 70%) of 2,2'-dinitro-4,4'-tetramethyldiaminodiphenylmethane was obtained in the form of orange-red crystals with a m.p. of 193° which closely agreed with the literature data. The product obtained displayed no melting point depression in a mixed sample with the pure substance. The diazo reaction did not disclose the presence of amino groups.

3. Reaction of 2-Nitroaniline with Formaldehyde. Preparation of 3,3'-Dinitro-4,4'-diaminodiphenylmethane

The reaction with 2-nitroaniline, conducted under the conditions described above and with the same quantitative relations, led to the formation (after analogous treatment and crystallization from glacial acetic acid) of a substance in the form of orange-red needles with a m.p. of 222-224°. The product obtained had a distinct diazo reaction and closely agreed in its properties (color, melting point) with those of 3,3'-dinitro-4,4'-diaminodiphenylmethane.

SUMMARY

The reciprocal reaction of the three isomeric nitroanilines with formaldehyde in a 100% formic acid medium was studied. It was shown that it is possible to obtain the following with excellent yields: 4-nitrodimethylaniline, 2,2'-dinitro-4,4'-tetramethyldiaminodiphenylmethane and 3,3'-dinitro-4,4'-diaminodiphenylmethane.

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*The student Bolgova participated in the experimental work.

** Consultant's Bureau Translation, p. 303.

Dipole Moments and Structure of Certain Sulfanilamide Compounds. p. 869.

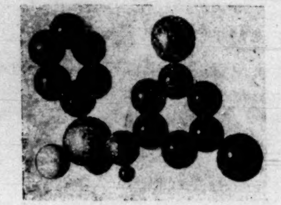


Fig. 2.

Dipole Moments and the Structure of Certain Acridine Derivatives. p. 875

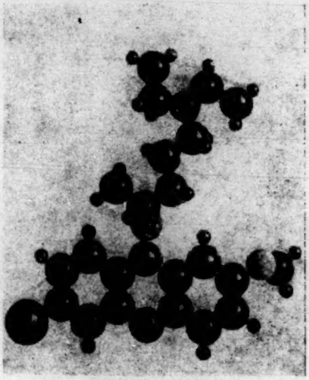


Fig. 1.

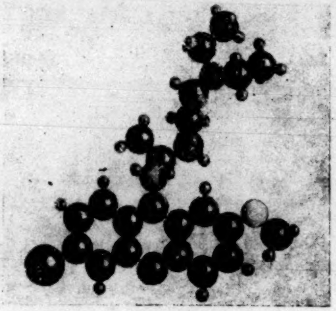


Fig. 2.

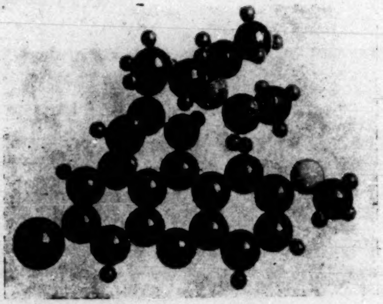
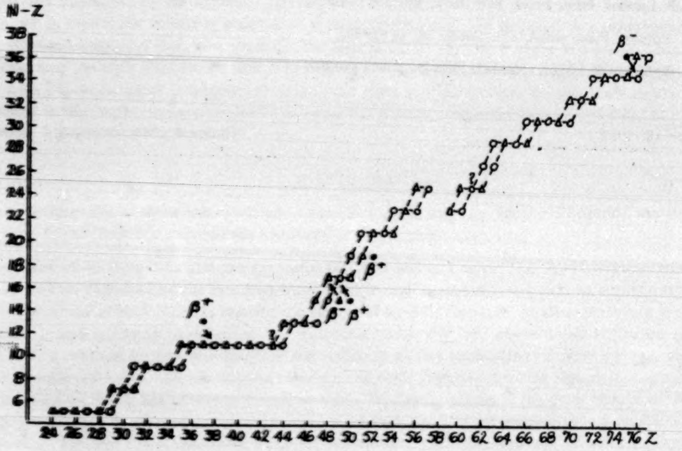


Fig. 4.

COMMENTS ON EXCEPTIONS TO THE SHCHUKAREV-MATTAUKH LAW

V. Simonov

Investigation of regularity in the isotopic system with respect to the isotopic nuclear number, i.e., the difference N−Z, revealed a characteristic order in the change of the number N−Z in relation to the Z-isotopes belonging to the nuclear types 4n + 1 and 4n + 3 [1], where n represents the quotient obtained by dividing the mass number of the nucleus A by four.



Relation between the isotopic nuclear number and the Z-isotopes. Open circle − stable 4n + 3 nucleus; open triangle − stable 4n + 1 nuclear type. Solid circles and triangles − radioactive nuclei.

The appearance of the regularity gives a formal rule for evaluation of the stability of nuclei having uneven A.

The relation between N−Z and Z is indicated in the figure.

It is easily observed that the distribution of these types of nuclei on the graph obeys a definite order which is expressed in the following form.

For a change of Z by two units, the number N−Z remains unchanged, i.e., for $\Delta Z = 2$, $\Delta(N-Z) = 0$, but for a change of Z by one unit the number N−Z changes by two units, i.e., for $\Delta Z = 1$, $\Delta(N-Z) = 2$.

A nucleus, satisfying this principle, joins the points of the line in such a way that the horizontal lines and the oblique lines, connecting nuclei of given type, do not change their directions, if nuclei of corresponding type lie along them. As a result we obtain a segmented line: horizontal-iso-differentials and pairs of oblique lines. These lines connect the well-known stable nuclei; therefore it is possible to call them stability lines. In the diagram it can be seen that elements of a given Z do not have more than two stable isotopes with uneven A. Those nuclei which belong to the 4n + 1 and 4n + 3 types, but do not satisfy the observed rule (they do not lie on the stability line), appear to be radioactive.

They are β^+ -active if they lie under the stability line, and ρ -active if they lie above the line.

According to the formal scheme considered, the isotopes In^{113}, Sn^{115} and Te^{123}, which appear to be isobars of Cd^{113}, In^{115} and Sb^{123}, respectively, should possess some type of radioactivity other than β^--activity. If the percentage content of isotopes of a given element seems to be of characteristic stability [2, 3, 4], then these isotopes, like isotopes of low percentage content, should refer to the unstable isotope.

According to G. Bete [5] this nucleus also directs the energetic instability. Thus, according to our considerations, the Shchukarev-Mattaukh Law should not have an exception; the isotopes In^{113}, Sn^{115} and Te^{123} should be radioactive. Our formal physical scheme finds clarification in the nuclear structure that we developed.

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INVESTIGATIONS OF NON-AQUEOUS SOLUTIONS

III. THE SYSTEM NAPHTHALENE–IODINE–MERCURIC BROMIDE

P. A. Smirnov

Systems that we investigated earlier, naphthalene–mercuric iodide [1] and naphthalene–iodine–mercuric chloride [2], enabled us to some extent, to predict the behavior of mercuric bromide and iodine in molten naphthalene. We showed that HgI_2 molecules in the presence of iodine in molten naphthalene undergo association, but $HgCl_2$ molecules react with iodine to form polyhalides. The different behavior of the HgI_2 and $HgCl_2$ molecules toward iodine was explained by the different polarization strengths of the I^- and Cl^- ions. Iodide ions from mercuric iodide and I_2 molecules mutually polarize in molten naphthalene. An increase, as a consequence of polarization, of the dipolar intensity of HgI_2 also promotes the association of the molecules of this salt. Chloride ions have a greater polarizing strength than iodide ions, which is why $HgCl_2$ molecules form complexes (polyhalides) with strongly polarized I_2 molecules. According to data in the literature [3], Cl^- and Br^- ions show similar polarization strengths, which is why $HgBr_2$ molecules should be expected to form complexes with I_2 molecules in molten naphthalene.

EXPERIMENTAL

We used iodine and naphthalene, purified as described previously [1]. Mercuric bromide was purified by recrystallization from alcoholic solution (by chilling).

The method of investigation and the apparatus are described in a report [1]. Previous experiment established that in molten naphthalene the reaction between $HgBr_2$ and I_2 proceeds as slowly as between $HgCl_2$ and I_2: equilibrium is attained after 7 hours of heating the system at 81-85°; therefore, in all experiments the solution of mercuric bromide and iodine in naphthalene was maintained at 81-85°, just above the solidification point, for 7 hours. The initial solution of mercuric bromide and iodine in molten naphthalene showed a black, and in transmitted light, a dark red color. On heating the solution, the color gradually became lighter, changing its tint, and acquiring the color of strong tea (a brownish-yellow tint). This phenomenon of the color change of the solution during heating indicated some reaction of the substance formed, the color of which differs from the color of the initial substance. Earlier [2] we conducted a control experiment of a 7-hour heating of iodine in naphthalene at 81-85°, which showed that iodine under the conditions of the experiment, was practically not volatilized.

In the present report, as in the two referred to above, two series of experiments were conducted.

First series. The solidification temperature of naphthalene (t) was determined. To a weighed portion of naphthalene, a weighed portion of $HgBr_2$ was added, and after a clear solution was obtained, the solidification temperature (t^1) was determined and the depression ($\Delta t_1 = t - t^1$) was calculated. Then a weighed portion of iodine was added to the solution of mercuric bromide in naphthalene; the solution was kept at a temperature of 81-85° for a period of 7 hours, after which the solidification temperature (t^2) was determined and the new depression value ($\Delta t_2 = t^1 - t^2$) was calculated.

Results of the first series of experiments are presented in Table 1.

Second series. The solidification temperature of naphthalene (t) was determined. To a weighed portion of naphthalene was added a weighed portion of iodine and, after obtaining a clear solution, the solidification temperature (t^1) was determined, and then the depression value ($\Delta t_1 = t - t^1$) was calculated. To the solution obtained, a weighed portion of $HgBr_2$ was added, the solution being kept at 81-85° for a period of 7 hours, after which the solidification temperature (t^2) was determined and the depression value, ($\Delta t_2 = t^1 - t^2$) was calculated.

Results of the second series of experiments are recorded in Table 2.

DISCUSSION OF RESULTS

First series of experiments. Calculations showed that the 0.0210 g weighed portion (in the first experiment) of iodine should produce a depression equal to 0.03°. According to experimental data this depression equalled 0.01°.

TABLE 1

Expt. No.	Weight of $HgBr_2$ (g)	Δt_1	Weight of I_2 (g)	Δt_2	Δt by calculation	$\Delta t - \Delta t_2$	Quantity of combined I_2 (g)	Combined I_2 converted to millimoles per 1000 g naphthalene
1	0.2000	0.23°	0.0210	0.01°	0.03°	0.02°	0.0147	2.9
2	0.2000	0.23	0.0280	0.01	0.04	0.03	0.0221	4.4
3	0.2000	0.23	0.0300	0	0.04	0.04	0.0294	5.8
4	0.2000	0.23	0.0350	0.01	0.05	0.04	0.0294	5.8
5	0.2000	0.23	0.0500	0	0.07	0.07	0.0500	9.9
6	0.0708	0.07	0.0500	0	0.07	0.07	0.0500	9.9

Note: The weighed portion of naphthalene in all experiments was 20 g.

TABLE 2

Expt. No.	Weight of iodine (g)	Δt_1	Weight of $HgBr_2$ (g)	Δt_2	Δt by calculation	$\Delta t - \Delta t_2$	Combined $HgBr_2$ (g)	Combined $HgBr_2$ converted to millimoles per 1000 g naphthalene
1	0.0210	0.03°	0.0300	0.01°	0.03°	0.02°	0.0209	2.9
2	0.0300	0.04	0.3000	0.25	0.29	0.04	0.0418	5.8
3	0.0300	0.04	0.3000	0.25	0.29	0.04	0.0418	5.8
4	0.0300	0.04	0.2000	0.17	0.19	0.02	0.0209	2.9
5	0.0500	0.07	0.0708	0.03	0.07	0.04	0.0418	5.8
6	0.0460	0.06	0.0400	0.02	0.04	0.02	0.0209	2.9
7	0.0500	0.07	0.2000	0.17	0.19	0.02	0.0209	2.9

Note: The weighed portion of naphthalene in all experiments was 20 g.

TABLE 3

Nos. of expts. of the 1st and 2nd series	Weight of iodine (g)	Weight of $HgBr_2$ (g)	Ratio of $I_2/HgBr_2$ (in millimoles)	Probable formula
1 I	0.0210	0.2000	2.9 : 2.9 = 1	$HgBr_2 \cdot I_2$
1 II	0.0210	0.0300		
2 I	0.0280	0.2000	4.4 : 2.9 = 1.5	$2HgBr_2 \cdot 3I_2$
4 II	0.0300	0.2000		
3 I	0.0300	0.2000	5.8 : 2.9 = 2	$HgBr_2 \cdot 2I_2$
4 II	0.0300	0.2000		
6 I	0.0500	0.0708	9.9 : 5.8 = 1.7 (?)	?
5 II	0.0500	0.0708		
5 I	0.0500	0.2000	9.9 : 2.9 = ~3.5	$2HgBr_2 \cdot 7I_2$
7 II	0.0500	0.2000		
6 I	0.0500	0.0708	9.9 : 2.9 = ~3.5	$2HgBr_2 \cdot 7I_2$
6 II	0.0460	0.0400		
4 I	0.0350	0.2000	5.8 : 2.9 = 2	$HgBr_2 \cdot 2I_2$
4 II	0.0300	0.2000		
3 I	0.0300	0.2000	5.8 : 5.8 = 1	$HgBr_2 \cdot I_2$
3 II	0.0300	0.3000		

Hence, it followed that the depression that should be produced by the combined quantity of iodine, if it remained free, amounted to $0.03-0.01 = 0.02$. From the value of this depression, the quantity of combined iodine (0.0147 g) was calculated, and then converted to the quantity per 1000 g of naphthalene, expressed in millimoles (2.9). If we divide the series of numbers of the last column of Table 1 by the least number, then we obtain: $2.9:2.9 = 1$, $4.4:2.9 = 1.5$, $5.8:2.9 = 2$, $9.9:2.9 = \sim 3.5$. The simple ratios of these numbers indicated that iodine formed a definite chemical compound with $HgBr_2$.

Second series of experiments. Figures in the last and next-to-last columns of Table 2 represent the quantity of combined $HgBr_2$, just as in the first series.

In the series of figures of the last column, the first (2.9), expresses the least number of millimoles of $HgBr_2$ combining with iodine. The last column of Table 1 also begins with this figure (2.9). Thus, the minimum quantity of millimoles of $HgBr_2$ and I_2 reacting (under our conditions) is identical. Considering the last column of Table 2, it is possible to see that $HgBr_2$ reacts with either 2.9 or 5.8 mmoles of iodine, i.e., the number is a multiple of 2.9. In other words, $HgBr_2$ reacts with the same number of millimoles, or the same multiple thereof, of iodine.

In Table 3 the experimental results given in Tables 1 and 2 are compared. For comparison, experiments in which either an identical or almost identical quantity of iodine and $HgBr_2$ was used were selected. Subscripts I and II in the first column of Table 3 designate, respectively, experiments of the first and second series.

The data of Table 3 led to a conclusion concerning the composition of the complexes formed by mercuric bromide and iodine. The probable formulas of these complexes are:

1) $HgBr_2 \cdot I_2$; 2) $2HgBr_2 \cdot 3I_2$; 3) $HgBr_2 \cdot 2I_2$; and 4) $2HgBr_2 \cdot 7I_2$.

Comparing these formulas with the formulas of the mercuric chloride polyhalides [2]:

$HgCl_2 \cdot I_2$	$HgBr_2 \cdot I_2$
$HgCl_2 \cdot 2I_2$	$HgBr_2 \cdot 2I_2$
$3HgCl_2 \cdot I_2$	–
$4HgCl_2 \cdot I_2$	–
–	$2HgBr_2 \cdot 3I_2$
–	$2HgBr_2 \cdot 7I_2$

it is seen that of the four polyhalides formed by mercuric bromide, only two have compositions analogous to the polyhalides formed by mercuric chloride.

SUMMARY

1. A cryoscopic investigation of the system naphthalene–iodine–mercuric bromide made possible the conclusion that $HgBr_2$ forms polyhalides with iodine.

2. The probable formulas of these polyhalides are:

$$HgBr_2 \cdot I_2,\ 2HgBr_2 \cdot 3I_2,\ HgBr_2 \cdot 2I_2 \text{ and } 2HgBr_2 \cdot 7I_2.$$

3. In two cases the formulas of the mercuric bromide polyhalides appeared to be analogous to the formulas of the mercuric chloride polyhalides.

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* See Consultants Bureau Translation, page 1135.

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SUMMARY

1. [illegible]

2. [illegible]

3. [illegible]

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ISOBARIC POTENTIALS OF FORMATION OF DIFFICULTLY-SOLUBLE OXIDE HYDRATES AND BASIC SALTS AND THE pH OF THE SOLUTIONS IN EQUILIBRIUM WITH THE SOLID PHASE

V. L. Kheifets and A. L. Rotinyan

Processes for separating metals, based on differences in the conditions of formation of their difficultly soluble hydrates or basic salts, occupy a greater and greater place both in analytical chemistry, and in the most diverse fields of engineering. A considerable number of reports [1-12, 14, 16] in recent years have been devoted to the present problem, and although they have essentially advanced the status of the problem, it nevertheless is still far from a final solution.

In the present report we thought it expedient to consider the general physico-chemical basis of processes of formation of difficultly soluble metal oxide hydrates and their basic salts.

By hydrolysis reactions, or by the action of alkaline reagents on solutions of the salts of many metals, the formation of difficultly soluble compounds is possible in principle: a) hydrates of the type $Me(OH)_n$, b) basic salts of simple metal salts and their hydrates of the type, $x[Me_bA_d]\cdot y[Me(OH)_n]$, and c) more complex combinations of hydrates and salts of two or more metals.

In each concrete case, that difficultly soluble compound will be formed first, the formation of which is accompanied by maximum decrease in isobaric potential; in other words the compound which has the least solubility.

Relation Between the Isobaric Potential of Formation of the Difficulty Soluble Hydrate of a Metal Oxide and the pH of the Solution

If one considers the system, metal oxide hydrate (solid phase)—solution, as an equilibrium, it is possible to write:

$$Me^{n+} + n\,OH' \rightleftharpoons Me(OH)n. \tag{1}$$

We employ the following designations:

ΔZ_1^0 – the standard isobaric potential of formation of $Me(OH)_n$ of the elements;

ΔZ_2^0 – the same value for the Me^{n+} ion;

ΔZ_3^0 – the same value for the OH' ion;

$\Delta Z_{hyd.}^0$ – standard isobaric potential for reaction (1).

Proceeding from reaction (1),

$$\Delta Z_2^0 + RT \ln a_{Me^{n+}} + n\Delta Z_3^0 + nRT \ln a_{OH'} = \Delta Z_1^0 + RT \ln a_{Me(OH)n}. \tag{2}$$

If the difficultly soluble hydrate occurs in the form of solid phase, i.e., under standard conditions, then $a_{Me(OH)_n} = 1$ and $RT \ln a_{Me(OH)_n} = 0$.

Designating the dissociation constant of water by K_W, equation (2) may be rewritten as:

$$pH = \frac{\Delta Z_1^0 - \Delta Z_2^0 - n\Delta Z_3^0}{2.3nRT} - \log K_W - \frac{1}{n}\log a_{Me^{n+}}. \tag{3}$$

From equation (3) it is seen that, knowing ΔZ_1^0, ΔZ_2^0 and ΔZ_3^0, it is possible to calculate the pH value corresponding to the equilibrium between hydrate (in the form of solid phase) and solution, for any activities of the metal ions.

On the other hand, since

$$\Delta Z^0_{hyd.} = -RT \ln K = RT \ln a_{Me^{n+}} a^n_{OH'} \tag{4}$$

we may transform equation (2) to

$$\Delta Z^0_1 = \Delta Z^0_2 + n\Delta Z^0_3 + \Delta Z^0_{hyd.} \tag{5}$$

Thus, the values of ΔZ^0_1, ΔZ^0_2 and ΔZ^0_3 or two of these three quantities and the equilibrium value of the pH of formation of the hydrate, enable one to calculate the standard isobaric potential of reaction (1).

Results of some calculations are presented in Table 1. For calculation $\Delta Z^0_3 = 37.58$ [13], is assumed.

TABLE 1

Standard Isobaric Potentials of Formation of Difficultly Soluble Oxide Hydrates (kcal/mole)

Formula of the hydrate	ΔZ^0_1 [13]	ΔZ^0_2 [13]	$\Delta Z^0_{hyd.}$ calculated from equation (5)	pH of formation of the hydrate calculated from equation (3)	pH of formation	
					hydrate according to Fialkov and Akselrud	compounds, according to Britton
$Co(OH)_3$	−142.00	28.90	−58.14	0.9	–	–
$Fe(OH)_3$	−166.30	− 2.53	−51.01	2.6	1.63	2
$Cu(OH)_2$	− 85.50	15.91	−26.24	4.5	4.21	5.3
$Zn(OH)_2$	−132.64	−35.17	−22.29	5.9	5.78	5.2
$Co(OH)_2$	−108.90	−12.80	−20.93	6.4	6.78	6.8
$Fe(OH)_2$	−115.66	−20.31	−20.18	6.7	5.62	5.5
$Cd(OH)_2$	−112.73	−18.55	−19.01	7.0	6.84	6.7
$Ni(OH)_2$	−105.60	−11.53	−18.90	7.1	6.70	6.7

The thermodynamic series of the pH of formation of the hydrates, as is easily observed, is identical with the series proposed by Akselrud and Fialkov [6] but is essentially preferable, because of its specificity, to the Britton [15] series. However, the series of pH of formation of the hydrates in any of its forms has much less value than is usually attributed to it, because in practice the basic salts of the metals, rather than the pure hydrates, usually form.

Relation Between the Isobaric Potential of Formation of Difficultly Soluble Basic Salt and the pH of the Solution

If, instead of a pure hydrate, a basic salt of composition $x[Me_bA_d]y[Me(OH)_n]$, is in equilibrium with the solution, then:

$$(y + bx)\,Me^{n+} + xd\,A^{m'} + ny\,OH' \rightleftharpoons x[Me_bA_d]y[Me(OH)_n], \tag{6}$$

here $\underline{m'} = \frac{nb}{d}$.

For equation (6), as previously, one may write:

$$(y + bx)\,\Delta Z^0_2 + RT \ln a^{y+bx}_{Me^{n+}} + xd\,\Delta Z^0_4 + RT \ln a^{xd}_{A^{m'}} + ny\,\Delta Z^0_3 + RT \ln a^{ny}_{OH'} =$$

$$= \Delta Z^0_5 + RT \ln a_{bas.} \tag{7}$$

Into equation (7) additional designations are introduced:

ΔZ^0_4 — standard isobaric potential of formation of anion salts of the elements;

ΔZ^0_5 — the same for formation of the basic salt from the elements;

$a_{bas.}$ — activity of the basic salt in the solid state, which at its maximum is assumed to equal unity.

Equation (7) is easily transformed to the following:

$$pH = \frac{\Delta Z_5^0 - (y + bx)\Delta Z_2^0 - xd\,\Delta Z_4^0 - ny\,\Delta Z_3^0}{2.3nyRT} - \frac{y + bx}{ny}\log a_{Me^{n+}} - \frac{xd}{ny}\log a_{A^{m'}} - \log K_W. \qquad (8)$$

Since,

$$\Delta Z_{bas.} = RT \ln a_{Me^{n+}}^{(y+bx)}\, a_{A^{m'}}^{xd}\, a_{OH'}^{ny}, \qquad (9)$$

where $\Delta Z_{bas.}$ is the standard isobaric potential of reaction (6), equation (7) may be written in the form:

$$(y + bx)\Delta Z_2^0 + xd\,\Delta Z_4^0 + ny\,\Delta Z_3^0 + \Delta Z_{bas.}^0 = \Delta Z_5^0. \qquad (10)$$

Depending on whether $RT \ln a_{Me^{n+}}\, a_{OH'}^{n} < RT \ln a_{Me^{n+}}^{(y+bx)}\, a_{A^{m'}}^{xb}\, a_{OH'}^{ny}$, the basic salt or pure hydrate will separate out in the precipitate.

From equations (9) and (4) it is clear that for an increase of activity of the salt in solution, a transition from formation of the hydrate to formation of basic salt is always inevitable; at the same time, a change of the value of x and y is possible, i.e., the formation of basic salts of different composition depends on the conditions.

For the basic salt the value of ΔZ_5^0 is unknown, therefore, calculation of $\Delta Z_{bas.}^0$ is possible only from experimental data on the pH of formation of the basic salt. Moreover, for calculation in each individual case it is necessary to know the coefficients x and y.

Mechanism Relating the pH of Formation of a Basic Salt to Its Composition and the Activities of Simple Salts in Solution

Equation (8) may be rewritten in the following form:

$$pH = \frac{\Delta Z_{bas.}^0}{2.3ny\,RT} - \frac{1}{ny}\log m_{Me^{n+}}^{(y+bx)}\,\gamma_{\pm}^{(y+bx)}\, m_{A^{m'}}^{xd}\,\gamma_{\pm}^{xd} - \log K_W. \qquad (11)$$

If there is no other salt having a common anion in the solution,

$$m_{Me^{n+}} = m_s b, \quad m_{A^{m'}} = m_s d \qquad (12)$$

(m_s is the molarity of the salt; $m_{Me^{n+}}$, $m_{A^{m'}}$ are the molarity of the ions). Then,

$$pH = \frac{\Delta Z_{bas.}^0}{2.3ny\,RT} - \frac{y + bx + dx}{ny}\log a_{\pm} - \frac{1}{ny}\log \frac{b^{(y+bx)}\,d^{xd}}{\left(b^{\frac{b}{b+d}}\,d^{\frac{d}{b+d}}\right)^{(y+bx+dx)}} - \log K_W. \qquad (13)$$

If we determine the pH of the solution which is in equilibrium with the solid phase at several activities of the salt, and construct a graph of pH $-\log a_{+}$ we may, by obtaining the angle of inclination of the straight line, easily determine the magnitudes of x and y, as the least integral number values. Thus, it appears feasible to calculate the standard isobaric potential of basic salt by measurements of the pH of the solutions in equilibrium with this salt.

Discussion of the Available Data on the Magnitude of the pH of Hydrate Formation

A large amount of experimental material on the magnitude of the pH of solutions in equilibrium with solid phase was obtained by Gromov, Fialkov and Akselrud, and by Patsenko.

In Fig. 1 are represented data of these authors for a series of zinc salts. Along the ordinate are values of the pH of the solution in equilibrium with solid phase, and along the abscissa axis, the logarithm of the average activity of the salt. The corresponding activity coefficients were taken from Harned and Owen [17]. The angular coefficients, obtained directly, equal 0.48-0.56, 0.84, 1.25 and 1.5. As seen from the figure, for small activities of salt, pure hydrate of $Zn(OH)_2$ forms, and in this case the pH of the hydrate formation actually does not depend on the nature of the anion of the salt.

Formation of pure hydrates in chloride and nitrate solutions occurred up to larger salt activities than in sulfate solutions. At large salt activities the basic salt forms, its composition depending on the nature of the anion. Cal-

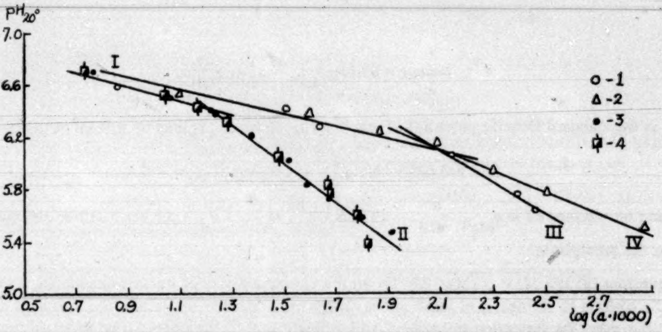

Fig. 1. Relation of pH of formation of hydrate or basic salt to the activity of a metal salt. [$ZnSO_4$. $ZnCl_2$. $Zn(NO_3)_2$]. 1 and 2) According to data [10]; 3) according to data [2]; 4) according to data [6]. I) $Zn(OH)_2$; II) $ZnSO_4 \cdot Zn(OH)_2$; III) $ZnCl_2 \cdot 2Zn(OH)_2$; IV) $Zn(NO_3)_2 \cdot 4Zn(OH)_2$.

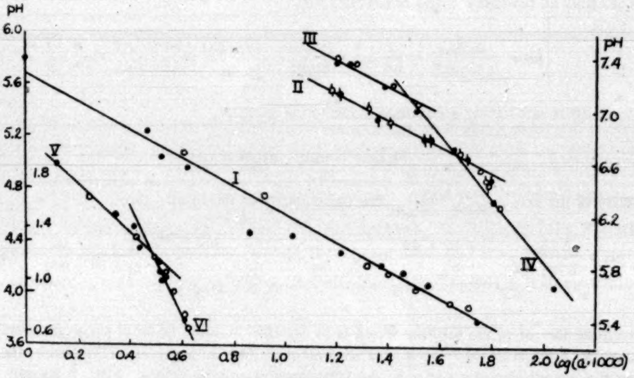

Fig. 2. Relation of pH of formation of the basic salt to the activity of the metal salt. Open circle — according to data [6]; solid circle — according to data [2]. Left external pH scale — for copper sulfate; left internal — for trivalent iron sulfate; right scale — for cadmium sulfate and divalent iron sulfate. I) $CuSO_4 \cdot 2Cu(OH)_2$; II) $FeSO_4 \cdot 2Fe(OH)_2$; III) $CdSO_4 \cdot 2Cd(OH)_2$; IV) $2CdSO_4 \cdot Cd(OH)_2$; V) $Fe_2SO_4)_3 \cdot Fe(OH)_3$; VI) $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$.

culation from formula (13) gives the following composition of basic salts: $ZnSO_4 \cdot Zn(OH)_2$, $ZnCl_2 \cdot 2Zn(OH)_2$ and $Zn(NO_3)_2 \cdot 4Zn(OH)_2$. In the region of stable formation of basic salt the nature of the anion and its valence, as would be expected, very strongly influence the magnitude of the pH of formation of the basic salt; therefore, confirmation of the independence from the nature of the anion, of the pH of formation of precipitates [10], as shown by the data of these authors, is justified only for the region of formation of pure hydrate, which is actually encountered very rarely.

In Fig. 2 data for some other metals are provided. As seen from the figure, copper at all concentration intervals studied gives only one compound – the basic salt $CuSO_4 \cdot 2Cu(OH)_2$ ($3CuO \cdot SO_3 \cdot 2H_2O$). At small salt activites cadmium also forms a similar compound. At large salt activities the less basic cadmium salt, $2CdSO_4 \cdot Cd(OH)_2$ ($3CdO \cdot 2SO_3 \cdot H_2O$), forms. The compounds formed from di- and tri-valent iron are of great interest. Unfortunately, we did not find in the literature any data on the activity coefficients for ferrous and ferric sulfates. We record below the results of all calculations carried out on the assumption that the activity coefficients of $FeSO_4$ solutions, at identical molarity, are equal to those for sulfates of other divalent metals, for instance, copper, zinc and cadmium. For $Fe_2(SO_4)_3$ we assumed that the activity of the salt was equal to the corresponding activity of the sulfates of trivalent metals, such as aluminum and indium [17]. With these assumptions it seems that divalent iron, within the concentration limits studied, should form only one compound, $FeSO_4 \cdot 2Fe(OH)_2$ ($3FeO \cdot SO_3 \cdot 2H_2O$).

Trivalent iron gives two compounds, $Fe_2(SO_4)_3 \cdot Fe(OH)_3$ and $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$ ($Fe_2O_3 \cdot 2SO_3 \cdot H_2O$ and $2Fe_2O_3 \cdot 5SO_3 \cdot H_2O$). The first of these compounds agrees with the compound observed by Posnjak and Merwin [18]. However, the anhydrous basic salt, $Fe_2(SO_4)_3 \cdot Fe(OH)_3$, is stable only at temperatures above 75°.

At lower temperatures the salts of the same composition with 4, 5, 6, 7 and 9 molecules of water of crystallization appear to be stable. The second compound of trivalent iron indicated above agrees with the basic salt $2Fe_2O_3 \cdot 5SO_3 \cdot 17H_2O$ (copiapite), if it is considered that at room temperature the basic salt $5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$ crystallizes with 16 molecules of water. Posnjak and Merwin point out that copiapite in contact with saturated solution is stable at temperatures below ~90°.

It should be pointed out that the composition of the solid phase, cited by Gromov, does not agree with the data presented above. Gromov gives one composition of the basic salt, $3Fe_2O_3 \cdot 2SO_3 \cdot H_2O$, for all concentration intervals of the salt.

A similar situation occurs also for the composition of basic salts of other metals, cited by Gromov.

Determining the compositions of some basic salts, we calculated the values of the standard isobaric potentials of their formation. Results of the calculations are given in Table 2. For the calculations we assumed the values $\Delta Z^0_{SO_4''} = -176.10$, $\Delta Z^0_{Cl'} = -31.33$, $\Delta Z^0_{NO_3'} = -26.25$. From data in the Table it is seen that the standard isobaric potentials of formation of the basic salts $\Delta Z^0_{bas.}$ are greater than $\Delta Z^0_{hyd.}$ for the pure hydrates. From values of $\Delta Z^0_{bas.}$ and the standard isobaric potential of formation of pure hydrate, $\Delta Z^0_{hyd.}$, one can determine the standard isobaric potentials of formation of the basic salt from the hydrate and simple salt $-\Delta Z^0_{simple}$. These values are recorded in the fourth column of Table 2.

TABLE 2

Standard Isobaric Potentials of Formation of Difficultly Soluble Basic Salts (kcal/mole).

Formula of basic salt	$\Delta Z^0_{bas.}$	ΔZ^0_{hyd}	ΔZ^0_{simple}
$ZnSO_4 \cdot Zn(OH)_2$	−27.95	−349.57	−5.66
$ZnCl_2 \cdot 2Zn(OH)_2$	−49.30	−367.82	−4.72
$Zn(NO_3)_2 \cdot 4Zn(OH)_2$	−94.70	−623.75	−5.54
$CuSO_4 \cdot 2Cu(OH)_2$	−60.50	−339.21	−8.02
$FeSO_4 \cdot 2Fe(OH)_2$	−47.20	−434.57	−6.84
$CdSO_4 \cdot 2Cd(OH)_2$	−45.60	−427.69	−7.58
$2CdSO_4 \cdot Cd(OH)_2$	−29.05	−512.07	−10.04
$Fe_2(SO_4)_3 \cdot Fe(OH)_3$	−73.00	−722.64	−21.98
$5Fe_2(SO_4)_3 \cdot 2Fe(OH)_3$	−196.00	−3093.37	−94.00

SUMMARY

1. We showed the feasibility of calculation of the standard isobaric potentials of formation of basic salts and pure hydrates from measurements of the pH of solutions in equilibrium with the solid phase of the basic salt or pure hydrate.

2. We worked with the experimental data available in the literature. It showed that in practically all cases at large concentrations the basic salts form. The compositions of these salts were determined. Pure hydrates form only in the case of zinc at small initial ionic concentrations.

3. For a series of metals, we calculated the standard isobaric potentials of the reaction of formation of basic salts from ions, elements, and also from the pure hydrates and simple salts.

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COMPLEX FORMATION AND DOUBLE DECOMPOSITION IN A RECIPROCAL SYSTEM OF SODIUM AND POTASSIUM PYROPHOSPHATES AND TUNGSTATES

M. L. Sholokhovich and A. G. Bergman

Investigation of a series of reciprocal systems of Na, K || MeO_4, P_2O_7 (where M = S, Cr, Mo, W) gave interesting material illustrating a series of differences in the chemical properties of sodium and potassium salts. Thus, it was established that potassium pyrophosphate forms eutectic mixtures with salts of the K_2MeO_4 type, whereas sodium pyrophosphate forms a eutectic mixture only with Na_2SO_4, while the other salts of this type form the compounds: $Na_4P_2O_7 \cdot 4Na_2CrO_4$, melting without decomposition at 916°; $Na_4P_2O_7 \cdot 2Na_2MoO_4$, also melting without decomposition, but at a lower temperature – 821°; and $Na_4P_2O_7 \cdot 2Na_2WO_4$, melting with decomposition at 767° [1].

Such diversity in the chemical properties of the sodium and potassium salts does not appear to be accidental, but corresponds to their positions in the Mendeleev periodic system. There are numerous examples showing that elements of the third horizontal row appear to be transitions between the elements of the main and secondary subgroup. Proceeding from this, it is impossible to consider the element, sodium, as an analog of potassium, but it is possible to assume a series of general properties of the copper sub-group. The expressed assumption may be illustrated by the following examples.

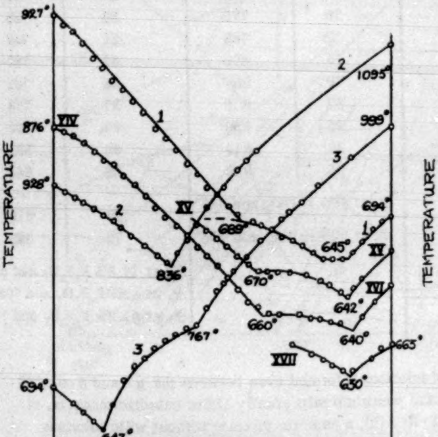

Fig. 1. Secondary side of the reciprocal system, Na, K || WO_4, P_2O_7 and internal sections XIV, XV, XVI, XVII through the reciprocal system. 1) $(K_2WO_4)_2$–$(Na_2WO_4)_2$; 2) $(K_2WO_4)_2$–$K_4P_2O_7$; 3) $(Na_2WO_4)_2$–$Na_4P_2O_7$.

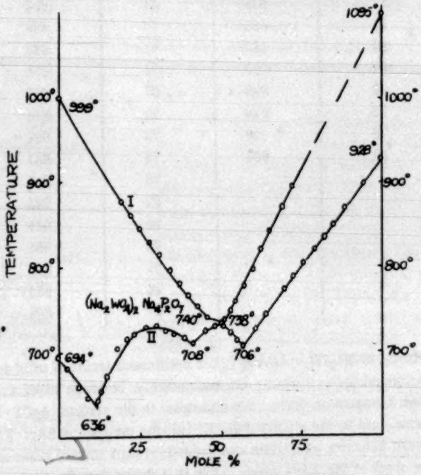

Fig. 2. Diagonal sections of the reciprocal system, Na, K || WO_4, P_2O_7. I) $Na_4P_2O_7$–$(K_2WO_4)_2$, II) $(Na_2WO_4)_2$–$K_4P_2O_7$.

1. The crystalline structures of monovalent compounds of sodium, copper and silver are similar, which also leads to the formation of a continuous series of solid solutions, for example, AgCl–NaCl [2], AgBr–NaBr [2]. In

TABLE 1

Binary Systems and Diagonal Sections. A) Initial component; B) added component. 1st column) Mole % B; 2nd column) temperature of appearance of first crystals.

1	2	1	2	1	2	1	2
A) $(Na_2WO_4)_2$	B) $Na_4P_2O_7$	A) $(K_2WO_4)_2$	B) $(Na_2WO_4)_2$	A) $Na_4P_2O_7$	B) $(K_2WO_4)_2$	A) $(Na_2WO_4)_2$	B) $K_4P_2O_7$
6	676	3	915	19	878	3	682
9	666	6	910	22	860	6	660
12	656	9	895	25	845	9	646
15	647	12	876	28	828	12	641
18	675	15	865	31	814	13	653
21	706	18	850	34	793	15	670
24	720	21	840	37	776	18	706
27	730	24	827	40	766	21	716
30	740	27	815	43	752	23	720
33	751	30	793	46	740	27	730
36	758	33	783	50	736	30	730
39	764	36	770	51	731	33	725
42	767	39	756	53	724	36	720
45	788	42	742	55	714	39	716
48	808	45	727	57	706	42	708
50	818	48	718	61	726	45	725
53	830	51	705	64	743	48	730
57	848	54	696	70	773	50	735
61	865	58	689	73	788	51	740
64	880	61	684	76	805	53	750
67	890	64	675	79	820	54	762
70	898	67	671	82	835	57	778
73	910	70	665	85	850	60	798
78	928	73	661	88	870	63	821
88	960	76	651	94	900	65	845
		79	645			—	—
		82	645			69	870
		85	645			72	896
		88	651				
		91	665				
		94	680				
		97	689				

P_1 at 46% K_2WO_4 and 740°

P_2 at 57% K_2WO_4 and 706°

P_1 at 11.5% $K_4P_2O_7$ and 636°

P_2 at 42% $K_4P_2O_7$ and 708°

P_3 at 51.5% $K_4P_2O_7$ and 738°

systems of $Na_2SO_4-Ag_2SO_4$ [2], a continuous series of solid solutions is formed even between the α- and β-modifications of these sulfates. On the contrary, between silver and potassium salts usually either eutectic mixtures, or even compounds, form. For example, in the system, AgCl–KCl [2], a eutectic mixture without solid solutions forms, and in the system AgI–KI [2], the compound 2AgI · KI, which melts with decomposition, forms. Such different behavior of sodium and potassium salts toward silver salts is of fundamental interest when we proceed from the sizes of the ionic radii. Thus it is shown that the ionic radius of silver (1.13-1.23 A) occupies a position intermediate between the ionic radii of potassium (1.33 A) and sodium (0.98 A).

2. The crystalline structures of the corresponding salts of sodium and potassium are different, as a result of which, on the whole, a series of systems of similar salts of sodium and potassium form either eutectic mixtures or compounds. Thus, in the $K_2WO_4-Na_2WO_4$ system that was investigated, no continuous series of solid solutions formed, but a formation of chemical compounds took place. In systems of sodium and potassium pyrophosphates, solid solutions form only in the liquidus systems, whereas in the solid phase, compounds [2] form, which clearly appeared in our investigation of the reciprocal systems of Na, K ‖ WO_4, P_2O_7.

EXPERIMENTAL

The investigation was carried out by the visual-polythermal fusion method. All data are reported as equimolar percentages. The salts required for the studies were: potassium pyrophosphate, obtained by decomposition of chemically pure disubstituted potassium phosphate, and potassium tungstate, obtained by fusion of chemically pure K_2CO_3 and $(NH_4)_2WO_4$, taken in stoichiometric proportions. The pyrophosphate and the sodium tungstate were analytically pure quality.

Binary systems. $(K_2WO_4)_2-K_4P_2O_7$ (Fig. 1) – eutectic. Eutectic at 34.5% $K_4P_2O_7$ and 836° $(Na_2WO_4)_2-Na_4P_2O_7$ (Table 1, Fig. 1) formed a chemical compound of 1:1 composition, melting with decomposition; transition point at 42% $Na_4P_2O_7$ and 767°. Eutectic at 15% $Na_4P_2O_7$ and 647°. $(K_2WO_4)_2-(Na_2WO_4)_2$, according to literature data [2], in the liquidus-solid solutions;and in the solidus, the 1:1 compound formed. According to our data (Table 1, Fig. 1) in the liquidus system the 1:1 compound forms, and it melts with decomposition at 55% Na_2WO_4 and 689°. In the interval from 79 to 86% Na_2WO_4 a discontinuity occurs, which probably indicates a compound there. However, this part of the diagram requires additional special study.

$Na_4P_2O_7-K_4P_2O_7$ was studied earlier [2, 3].

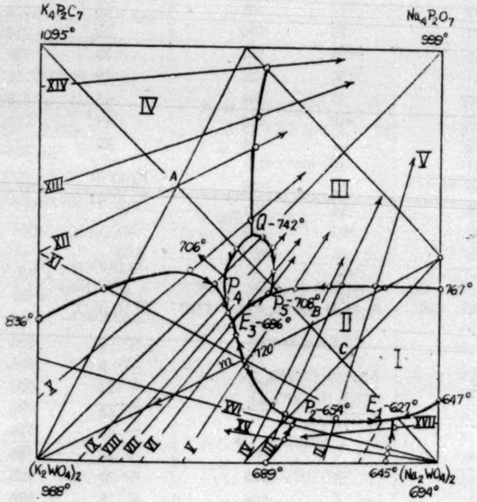

Fig. 3. Crystallization surface of the reciprocal system Na, K || WO_4, P_2O_7 with indication of the investigated sections as well as the triangulation section. Elucidation in text.

Diagonal profiles. (Table 1, Fig. 2) – both intersect, apart from the area of components, the area of the compound $Na_4P_2O_7 \cdot K_4P_2O_7$, exists in the system up to 742°; the $(Na_2WO_4)_2-K_4P_2O_7$ section also intersects the $Na_4P_2O_7 \cdot (Na_2WO_4)_2$ area.

Internal sections through the system. We studied 17 sections, locations of which are shown in Fig. 3, and data given in Table 2 and in Figs. 1, 4 and 5.

Of special interest in the system is the part of the diagram where the fusions are enriched in sodium and potassium tungstate. Here (Figs. 3 and 6) appears clearly the chemical compound $Na_2WO_4 \cdot K_2WO_4$, passed over earlier in the binary system [2]. The dotted line records the region in which we established the possibility of the existence of binary phases in the binary system $K_2WO_4-Na_2WO_4$. However, the profile of this phase was not made apparent. This part of the diagram requires further investigation.

Projection of the three-dimensional diagram of the reciprocal system onto the composition square (Fig. 6) indicates the formation of 7 zones of crystallization in the system (Table 3).

All isotherms (except the 720° isotherm) were determined for every 50°.

The form of the region completed by the binary descent point Q (Fig. 6) and the character of the 720° isotherm inside this region indicate that, in the region being considered, a compound crystallizes, the terminal of which corresponds to the composition, $K_4P_2O_7 \cdot Na_4P_2O_7$.

TABLE 2

A) Initial mixture; B) added component. 1st column) Mol. % B; 2nd column) temperature of appearance of first crystals

Section I

A) [50% $(Na_2WO_4)_2$ + 50% $Na_4P_2O_7$]; B) $(K_2WO_4)_2$

1	2
0	820
5	782
8	765
12	752
15	742
18	753
20	757
25	762
30	762
35	762
40	750
45	736
48	726
50	720
53	730
55	740

P_1 at 15% K_2WO_4, 742°
P_2 at 50% K_2WO_4, 720°

Section II

A) [30% $(K_2WO_4)_2$ + + 70% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	667
2	662
4	654
6	650
8	644
10	640
15	682
20	714
25	730
30	746
35	751
40	747
45	750
50	772
55	794
60	818
65	839
70	860
75	880

P_1 at 11.5% $Na_4P_2O_7$, 637°
P_2 at 42.5% $Na_4P_2O_7$, 742°

Section III

A) [45% $(K_2WO_4)_2$ + + 55% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	696
4	688
6	680
8	672
10	666
12	666
15	683
20	703
25	727
30	747
35	754
38	752
41	743
45	738
47	747
50	760
55	780
60	804
65	828

P_1 at 11.5% $Na_4P_2O_7$, 662°
P_2 at 43% $Na_4P_2O_7$, 716°

Section IV

A) [50% $(K_2WO_4)_2$ + + 50% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	718
2	716
4	709
8	693
10	685
15	670
20	703
25	733
30	753
35	752
40	740
43	734
45	748
50	765

P_1 at 14.5% $Na_4P_2O_7$, 664°
P_2 at 42% $Na_4P_2O_7$, 728°

Section V

A) [65% $(K_2WO_4)_2$ + + 35% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	780
4	778
6	776
8	772
10	770
12	760
15	746
17	736
20	720
25	720
30	728
35	730
40	720
41	716
45	731
50	750
55	771
60	788
65	807

P_1 at 22% $Na_4P_2O_7$, 706°
P_2 at 41.5% $Na_4P_2O_7$, 716°

Section VI

A) [75% $(K_2WO_4)_2$ + + 25% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	825
4	815
6	809
8	799
10	789
12	781
15	775
20	755
25	730
30	720
33	718
35	717
37	716
40	710
43	715
45	725
50	744

P_1 at 30% $Na_4P_2O_7$, 718°
P_2 at 41.5% $Na_4P_2O_7$, 706°

Section VII

A) [80% $(K_2WO_4)_2$ + + 20% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	844
5	830
10	808
15	787
20	766
25	746
30	730
33	716
36	716
39	720
42	716
45	715
48	730
50	737

P_1 at 34.5% $Na_4P_2O_7$, 712°
P_2 at 45.5% $Na_4P_2O_7$, 714°

Section VIII

A) [85% $(K_2WO_4)_2$ + + 15% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	865
5	830
10	808
15	785
20	765
25	745
30	725
36	690
39	708

P at 36% $Na_4P_2O_7$, 690°

Section IX

A) [90% $(K_2WO_4)_2$ + + 10% $(Na_2WO_4)_2$]; B) $Na_4P_2O_7$

1	2
0	885
2	875
4	870
6	860
8	850
10	840
12	825
15	815
20	787

Section IX

1	2
25	765
30	740
35	720
38	710
41	700
44	712
50	730
52	733
54	747
55	755
60	776

P_1 at 41% $Na_4P_2O_7$, 700°
P_2 at 52.5% $Na_4P_2O_7$, 735°

Section X

A) [85% $(K_2WO_4)_2$+ + 15% $K_4P_2O_7$]; B) $Na_4P_2O_7$

1	2
0	896
5	880
10	855
15	830
20	808
25	783
30	755
35	745
36	725
39	730
42	735
45	740
48	745
50	745
53	758
55	773
60	792
65	808

P_1 at 36% $Na_4P_2O_7$, 725°
P_2 at 51.5% $Na_4P_2O_7$, 748°

Section XI

A) [50% $(K_2WO_4)_2$ + + 50% $K_4P_2O_7$]; B) Na_2WO_4

1	2
0	930
5	900
10	869
15	820
16.5	800
20	793
23	792
25	791
27	789
30	782
33	777
35	773
40	758
43	751
45	743
48	731
52	722
55	720
58	717
61	708
65	700

P_1 at 17% Na_2WO_4, 792°
P_2 at 49.5% Na_2WO_4, 720°

Section XII

A) [50% $(K_2WO_4)_2$ + + 50% $K_4P_2O_7$]; B) $Na_4P_2O_7$

1	2
35	840
40	820
45	808
50	794
55	799
60	818
65	840

P at 52.5% $Na_4P_2O_7$, 790°

Section XIII

A) [35% $(K_2WO_4)_2$ + 65% $K_4P_2O_7$]; B) $Na_4P_2O_7$

1	2
0	990
5	970
10	954
15	936
20	918
25	900
30	880
33	869
36	860
39	854
42	845
45	838
48	834
55	834
60	852
65	870

P at 52.5% $Na_4P_2O_7$, 822°

Section XIV

A) [10% $(K_2WO_4)_2$ + 90% $K_4P_2O_7$]; B) $Na_4P_2O_7$

1	2
9	1050
15	1000
25	950
30	930
36	915
39	900
42	890
45	885
46	878
50	870
53	862
56	860
58	866
60	875
65	886
68	899

P at 55.5% $Na_4P_2O_7$, 858°

Section XV

A) [85% $(K_2WO_4)_2$ + 15% $K_4P_2O_7$]; B) $(Na_2WO_4)_2$

1	2
45	718
48	708
51	698
54	689
57	680
60	670
63	670
66	670
69	670
74	666
78	660
81	656
84	646
86	642
88	651
91	652

P_1 at 60% Na_2WO_4, 670°
P_2 at 86% Na_2WO_4, 642°

Section XVI

A) [75% $(K_2WO_4)_2$ + 25% $K_4P_2O_7$]; B) $(Na_2WO_4)_2$

1	2
0	876
3	872
6	868
9	859
12	849
15	839
18	834
21	820
24	812
27	797
30	783
33	775
36	764
39	753
42	737
45	727
48	717
51	704
54	690
57	675
60	670
63	661
66	661
72	661
75	656
78	656
81	652
84	652
91	658
95	676

P_1 at 61% Na_2WO_4, 660°
P_2 at 88% Na_2WO_4, 640°

Section XVII

A) [90% $(Na_2WO_4)_2$ + 10% $Na_4P_2O_7$]; B) $(K_2WO_4)_2$

1	2
0	665
3	662
6	648
12	637
15	637
18	640
21	648
24	653
30	666

P at 12.5% K_2WO_4, 630°

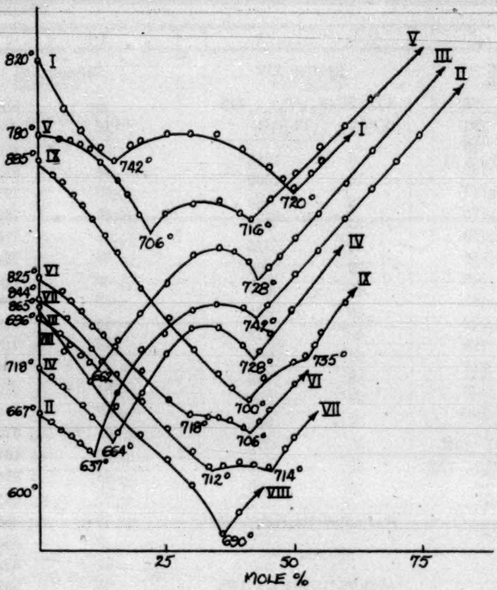

Fig. 4. Internal sections of the system Na, K || WO_4, P_2O_7.

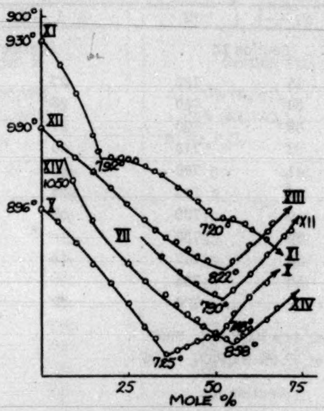

Fig. 5. Internal sections of the system, Na, K || WO_4, P_2O_7

The binary compound, $Na_4P_2O_7 \cdot (Na_2WO_4)_2$, within the reciprocal system, and melting with decomposition, is converted to a compound melting without decomposition and, existing in the system to the lowest temperature, it enters into the composition of the phase complexes during the final crystallization of the system at points E_1 and E_2.

In Figs. 7 and 8 a projection of the crystallization surface of the system onto the $K_2WO_4-Na_2WO_4$ and $K_4P_2O_7-(K_2WO_4)_2$ sides is provided.

TABLE 3

Area No.	Area of crystallization	Area of the considered region (in % of the total surface of crystallization of the system)
1	$K_4P_2O_7$	32.46
2	K_2WO_4	22.05
3	$Na_4P_2O_7$	26.03
4	Na_2WO_4	1.12
5	$K_2WO_4 \cdot Na_2WO_4$	2.41
6	$Na_4P_2O_7 \cdot (Na_2WO_4)_2$	14.78
7	$K_4P_2O_7 \cdot Na_4P_2O_7$	1.15

DISCUSSION OF RESULTS

A graphical examination of the system showed the effect of the secondary side of the system on the double decomposition reactions. We saw (Fig. 3) that neither one of the diagonal profiles participates in any part of the triangulation system. The square underwent division into 5 ternary systems, according to the scheme of Fig. 3* of the four-fold intersection, arising from the terminals of the binary compounds. Section I was stable. In agreement with these divisions, we have designated below the following ternary systems and their corresponding invariant points (Table 4):

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* In Fig. 3 the phase triangles are numbered with Roman numerals. The section profiles are shown in heavy lines.

I) $(Na_2WO_4)_2-(K_2WO_4)_2 \cdot (Na_2WO_4)_2-Na_4P_2O_7 \cdot (Na_2WO_4)_2$;

II) $(K_2WO_4)_2 \cdot (Na_2WO_4)_2-(K_2WO_4)_2-Na_4P_2O_7 \cdot (Na_2WO_4)_2$;

III) $(K_2WO_4)_2-Na_4P_2O_7 \cdot K_4P_2O_7-Na_4P_2O_7 \cdot (Na_2WO_4)_2$;

IV) $(K_2WO_4)_2-K_4P_2O_7-Na_4P_2O_7 \cdot K_4P_2O_7$;

V) $K_4P_2O_7 \cdot Na_4P_2O_7-Na_4P_2O_7-Na_4P_2O_7 \cdot (Na_2WO_4)_2$.

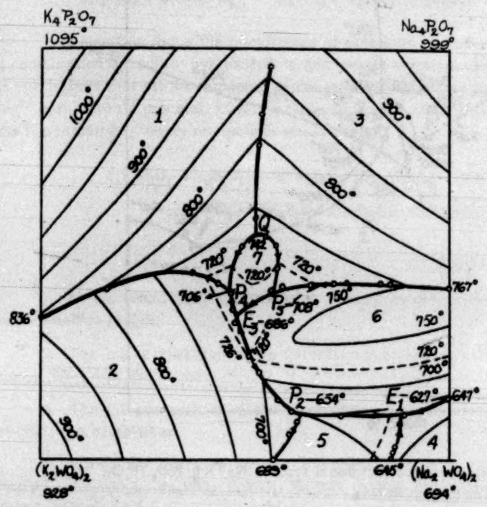

Fig. 6. Surface of crystallization of the reciprocal system, Na, K ‖ WO_4, P_2O_7. 1) $K_4P_2O_7$; 2) K_2WO_4; 3) $Na_4P_2O_7$; 4) Na_2WO_4; 5) $K_2WO_4 \cdot Na_2WO_4$; 6) $K_4P_2O_7 \cdot (Na_2WO_4)_2$; 7) $K_4P_2O_7 \cdot Na_4P_2O_7$.

The reaction between the initial components, in all cases, led to the formation of the chemical compounds of the secondary side.

The fundamental chemical interaction may be expressed below by the following three equations, corresponding to the three compositions on the $K_4P_2O_7-(Na_2WO_4)_2$ diagonal. These compositions are designated on the square by the letters A, B and C, and correspond to the intersection of the triangulation sections with this diagonal (Fig. 3).

A. $2K_4P_2O_7 + (Na_2WO_4)_2 = (K_2WO_4)_2 + K_4P_2O_7 \cdot Na_4P_2O_7$;

B. $K_4P_2O_7 + 2(Na_2WO_4)_2 = (K_2WO_4)_2 + Na_4P_2O_7 \cdot (Na_2WO_4)_2$;

C. $K_4P_2O_7 + 3(Na_2WO_4)_2 = 2[K_2WO_4 \cdot Na_2WO_4] + Na_4P_2O_7 \cdot (Na_2WO_4)_2$.

It was seen that, in the first and second case, paragenesis (coexistence) of potassium tungstate, with both pyrocompounds, and with sodium tungstate and pyrophosphate, occurred. In the third equation, which corresponds to point C, a

TABLE 4

Nature of the point	Composition (%)			Equilibrium phases
	$K_4P_2O_7$	Na_2WO_4	K_2WO_4	
E_1 ternary eutectic.	11.0	87.5	1.5	Na_2WO_4; $K_2WO_4 \cdot Na_2WO_4$; $Na_4P_2O_7 \cdot (Na_2WO_4)_2$
P_2 ternary transition.	10.5	63.0	26.5	K_2WO_4; $K_2WO_4 \cdot Na_2WO_4$; $Na_4P_2O_7 \cdot (Na_2WO_4)_2$
E_3 ternary eutectic.	35.0	48.0	17.0	K_2WO_4; $K_4P_2O_7 \cdot Na_4P_2O_7$; $Na_4P_2O_7 \cdot (Na_2WO_4)_2$
P_4 ternary transition.	41.0	45.5	13.5	K_2WO_4; $K_4P_2O_7$; $K_4P_2O_7 \cdot Na_4P_2O_7$
P_5 ternary transition.	41.0	57.5	1.5	$Na_4P_2O_7$; $K_4P_2O_7 \cdot Na_4P_2O_7$; $Na_4P_2O_7 \cdot (Na_2WO_4)_2$
E − binary eutectic	24.5	50.5	25.0	K_2WO_4; $Na_4P_2O_7 \cdot (Na_2WO_4)_2$

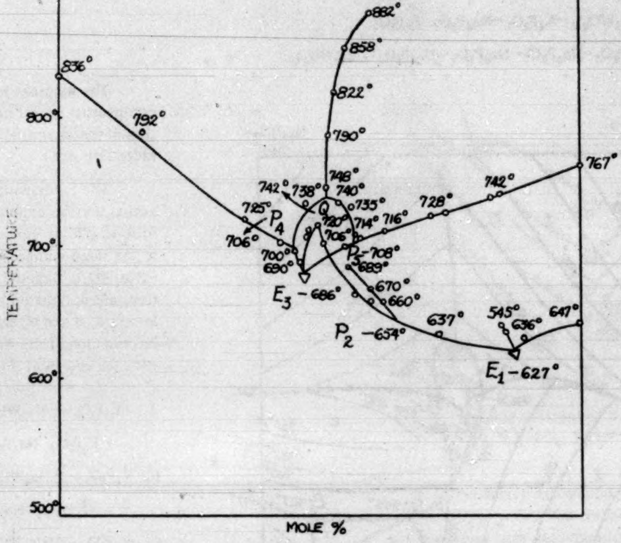

Fig. 7. Projection of the crystallization of the reciprocal system, Na, K|| WO_4, P_2O_7 onto the $K_4P_2O_7-(K_2WO_4)_2$ side. Elucidation in text.

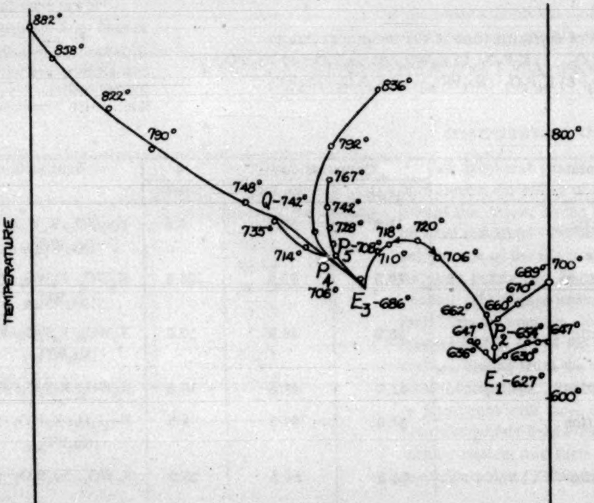

Fig. 8. Projection of the crystallization of the reciprocal system, Na, K|| WO_4, P_2O_7 on the $(K_2WO_4)_2-(Na_2WO_4)_2$ side. Elucidation in text.

stable mixture of sodium and potassium tungstates with sodium tungstate and pyrophosphate was obtained.

For the center of the square, where both diagonals intersect, we have the following equation which may be obtained by addition of Equations A and B.

$$\begin{array}{c}
2K_4P_2O_7 + (Na_2WO_4)_2 = (K_2WO_4)_2 + K_4P_2O_7 \cdot Na_4P_2O_7 \\
K_4P_2O_7 + 2(Na_2WO_4)_2 = (K_2WO_4)_2 + Na_4P_2O_7 \cdot (Na_2WO_4)_2 \\
\hline
3K_4P_2O_7 + 3(Na_2WO_4)_2 = 2K_2WO_4 + K_4P_2O_7 \cdot Na_4P_2O_7 + Na_4P_2O_7 + Na_2WO_4)_2
\end{array}$$

This equation shows the coexistence of potassium tungstate with pyrophosphate compounds, as well as with a combination of sodium pyrophosphate and sodium tungstate. From the character of the triangulation system, it also follows that all 3 compounds of the secondary side may not be paragenetic. For all interactions, the following reaction would proceed, in which the compound $Na_2WO_4 \cdot K_2WO_4$ would separate and the relationship between the two remaining binary compounds would change:

$$3[K_4P_2O_7 \cdot Na_4P_2O_7] + 3[Na_4P_2O_7 \cdot (Na_2WO_4)_2] + [3(K_2WO_4)_2 \cdot (Na_2WO_4)_2] =$$
$$= 8K_2WO_4 + 2[K_4P_2O_7 \cdot Na_4P_2O_7] + 5[Na_4P_2O_7 \cdot (Na_2WO_4)_2].$$

SUMMARY

1. By the visual-polythermal fusion method, the fusion diagram of the reciprocal system, $Na, K \parallel WO_4, P_2O_7$, was studied at length.

2. The 1:1 composition of the combination of sodium tungstate and pyrophosphate, melting with decomposition at 767°, was established.

3. The 1:1 composition of the combination of sodium and potassium tungstate, melting with decomposition at 689°, was established.

4. Within the reciprocal system, the crystallization boundaries of the components and the compounds, $Na_4P_2O_7 \cdot (Na_2WO_4)_2$, $Na_2WO_4 \cdot K_2WO_4$, $Na_4P_2O_7 \cdot K_4P_2O_7$ were established. The $Na_4P_2O_7 \cdot K_4P_2O_7$ area exists in the system only at 742°.

5. In the system, 5 ternary invariant points, one binary transfer invariant point, and one binary slope point, were established.

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* See Consultants Bureau Translation, page 605.

** See Consultants Bureau Translation, page 1331.

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SUMMARY

[illegible]

1. [illegible]

2. [illegible]

3. [illegible]

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LITERATURE CITED

(1) [illegible]

(2) [illegible]

(3) [illegible]

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TRANSITION OF H-ALUMINOSILICATES TO Al-ALUMINOSILICATES

K. G. Miesserov

Treatment of the aluminosilicates with solutions of mineral acids leads to displacement of the cations by hydrogen ions. The H-aluminosilicates forming are not stable and are easily converted to Al-aluminosilicates because of the aluminum contained in the aluminosilicates [1]. For natural bentonite this transition is accomplished both because of free aluminum oxide and because of the aluminum of the hydrargillite layers, and appears to be a result of the interaction of the hydroxyl groups of the tetrahedral Si—O layers with the hydroxyl groups occurring with the aluminum atoms [2].

The purpose of the present investigation is a study of the process of the displacement of aluminum ions by hydrogen ions in silica gel, activated aluminum oxide, and industrial synthetic aluminosilicates.

EXPERIMENTAL

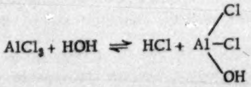
Samples of aluminosilicate were prepared by treatment of duplicate weighed portions of finely porous, ground silica gel with a 1 N solution of $AlCl_3$, partially neutralized by a solution of NaOH. After washing off the chloride ions with water, half the samples were dried and calcined. Then for the two samples (the calcined and the non-calcined) the exchange (by NaCl) and the hydrolytic (by CH_3COONa) acidities were determined.

In order to determine the exchange and hydrolytic acidities of the aluminosilicates, a method differing somewhat from the method employed for study of soil acidity [3, 4] was used. The method was developed for the following samples: industrial synthetic aluminosilicate catalysts, activated bentonite (industrial tableted catalyst, obtained by treating natural bentonite clays with acid), finely porous silica gel and activated aluminum oxide. All the samples were calcined at 500°. Duplicate weighed portions (5 g) of ground samples (particle size 0.5 mm) were repeatedly treated, by shaking with 60 ml of a 1 N solution of sodium chloride. The solutions were decanted into measuring flasks. The acidity of the salt extract was determined by titration of 25 ml of solution with 0.03 N NaOH in the presence of phenolphthalein (Table 1).

It is seen that the maximum value of the exchange acidity is attained by samples treated with 1 N solution of NaCl, in a period of 2 days, with a total solution volume of 500 ml. Values of the hydrolytic acidity for synthetic aluminosilicate and for alumino silica gel increased continuously with an increase of the period of treatment with sodium acetate solution. Apparently, this phenomenon depends on the fact that, in the sodium acetate solution, aluminum ions connected to the non-displaced centers were also converted (earlier [5] it was shown that at such a non-replaced center the single hydroxyl groups of silica gel appear). Thus, treatment of the two samples described with a solution of sodium acetate did not yield the actual value of the hydrolytic acidity. For activated bentonite and for silica gel, the maximum value of the hydrolytic acidity was attained by treatment with a solution of sodium acetate for a period of days up to a total solution volume of 500 ml.

The samples which were not treated with a solution of sodium chloride, were subjected to repeated treatment with a 1 N solution of HCl, and after careful washing away of the acid, were treated with solutions of NaCl and CH_3COONa to determine their exchange and hydrolytic acidities. In the hydrochloric acid extracts, the aluminum content was determined electrometrically by the Treadwell method [6] as modified by Chernov [7] (Table 2).

The data in Table 2 show that calcination of the alumino-silica gel leads to a decrease of the magnitude of its hydrolytic acidity. The reason for this phenomenon, apparently, depends on the following considerations. According to Chernov [7], in aqueous solutions of $AlCl_3$ at small concentrations, the first stage of hydrolysis takes place according to the equation



$$AlCl_3 + HOH \rightleftharpoons HCl + Al(Cl)_2(OH)$$

TABLE 1

Effect of Repeated Treatment of Aluminosilicate and Silica Gel with N Solutions of NaCl and CH_3COONa and Effect of the Total Volume of Solution on the Magnitude of the Exchange and Hydrolytic Acidities

Samples		Synthetic aluminosilicate					Activated bentonite			
Total volume of salt solution (ml)		250	500			1000	500			1000
Continuous treatment (days)		2	1	2	3	2 weeks	1	2	4	2 weeks
Acidity (mequiv/100 g) by treatment	NaCl solution	16.6	17.0	18.0	18.0	18.0	8.4	9.6	9.2	9.6
	CH_3COONa solution	44.0	46.2	51.0	54.0	61.2	28.2	28.8	28.8	28.8

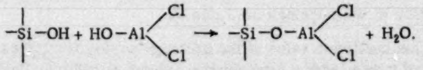
TABLE 2

Change of the Exchange and Hydrolytic Acidities of Calcined and Non-Calcined Samples of Alumino-Silica Gel As a Result of Their Treatment with a Normal Solution of Hydrochloric Acid (Values expressed in mequiv./100 g)

Sample of alumino-silica gel	Initial			Treated by 1 N solution of HCl			
	acidity		aluminum content	acidity		quantity of aluminum	
	exchange	hydrolytic		exchange	hydrolytic	separating in solution	remaining in sample
Non-calcined. . .	23.0	70.8	228	0	26.7	225	3
Calcined	24.0	56.6	228	6.6	33.6	140	88

Note: The content of aluminum in the initial samples was determined by boiling after treatment with a 1 N solution of HCl, and then determining the aluminum in the hydrochloric acid extract by the electrometric method of Treadwell.

Apparently, the interaction of the basic aluminum salt, formed from the OH groups of silica gel, proceeds according to the reaction



$$-\overset{|}{\underset{|}{Si}}-OH + HO-Al\begin{matrix}Cl\\Cl\end{matrix} \rightarrow -\overset{|}{\underset{|}{Si}}-O-Al\begin{matrix}Cl\\Cl\end{matrix} + H_2O.$$

Transition of the aluminum ions to the solid phase accompanies replacement, as a result of hydrolysis, of the remaining Cl^- ions by OH groups. Then in their turn, Cl^- ions interact with the hydroxyl groups of silica gel, with the liberation of water and formation of the Si−O−Al bond. The fact that treatment of like samples with a solution of a neutral salt depends, as shown experimentally, on the displacement in solution of only the trivalent aluminum ions, and the $NaNO_3$ extract of the samples did not contain chloride ions, may serve as confirmation of the stated mechanism. During treatment of silica gel with a solution having a large content of the basic form of aluminum, part of the OH^- groups may also remain with the aluminum atoms, as a result of the fact that in the vicinity of these atoms there are no free hydroxyl groups from silica gel. Actually, in the NaCl-extract of such samples, besides trivalent aluminum, there is a considerable quantity of its basic form.

The quantity of the basic form of aluminum was calculated by difference of the total aluminum content in solution and the content of trivalent aluminum ions. The quantity of the latter was determined by direct titration of the salt extract with a solution of alkali, in the presence of phenolphthalein. The total content of aluminum was determined by the Sokolov method [8], in which by addition of a small excess of hydrochloric acid all the basic form of aluminum in solution is converted to $AlCl_3$.

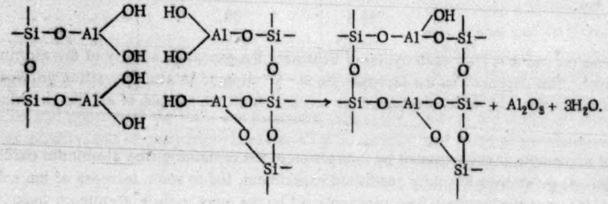
Aluminum atoms, with which unreacted hydroxyl groups remained, are retained by silica gel less firmly than trivalent aluminum ions, since their bonding with silica gel is accomplished by only one or two valences, depending on the number of hydroxyl groups remaining with the aluminum atoms, while the trivalent ions are fixed on silica gel by three valence bonds.

It is very probable that for this reason sodium acetate is capable of displacing such aluminum atoms in solution, even in the case where the aluminum ion replaces hydrogen ion in the hydroxyl group [5]. The calcined samples, containing the chemically bound basic form of aluminum, lead in all probability, to firmer attachments

TABLE 1 (continued)

Silica gel, activated aluminum oxide					Finely porous silica gel				
250		500			250		500		
1	2	1	2	3	1	2	1	2	3
17.1	19.5	20.4	24	24	—	—	—	1.8	—
46.5	49.2	51.0	52.8	53.4	19.8	19.8	25.2	25.2	25.2

of aluminum, as a result of the splitting off of part of the basic form of aluminum and formation of two or three valence bonds of the remaining aluminum with silica gel according to the scheme



From data of Table 2 it is seen also that treatment of the non-calcined samples with 1 N solution of HCl was accompanied by complete (within the limits of experimental error) removal of all the absorbed silica gel aluminum, and the magnitude of the exchange acidity was made equal to zero.

Extraction of all the aluminum from the calcined samples, treated with acid in the cold, was not successful. Obviously, this circumstance depended on the fact that the absorbed form of basic aluminum, on calcination yielded aluminum oxide. The latter, as a result of its poor solubility in cold hydrochloric acid solution, was not removed completely from the sample. Since in alumino-silica gel, after treatment with a 1 N solution of acid, no chemically bound aluminum remained, the preservation of some exchange capacity of the calcined sample treated with acid may be explained by the fact that it contained free aluminum oxide. The appearance of the exchange acidity under the influence of aluminum oxide, according to the point of view of Hansford [9] depends on the fact that aluminum oxide assumes part of the affinity of the oxygen atom of the silica gel hydroxyl group, as a result of which the bond between O and H loosens, and the mobility of the hydrogen ion increases.

The description enables one to conclude that the transition of H-alumino-silica gel to Al-alumino-silica gel is possible only because of the free aluminum oxide remaining in the samples after treatment with acid.

Results of further experiments are given in Table 3. The method of these experiments included the following: duplicate weighed portions of ground samples of activated bentonite, industrial synthetic aluminosilicate and alumino-silica gel were subjected to repeated treatment with a N solution of hydrochloric acid. The acid was then washed from the samples with water, they were dried, calcined and treated with a solution of sodium c chloride to determine the magnitude of the exchange acidity.

In the salt extract, besides the total acidity, the aluminum content was also determined. The Sokolov [8] method was used for the determination.

According to this method, two titrations with alkali in the presence of phenolphthalein were carried out: one titration without addition of NaF to the solution, which determines the total acidity of the solution, and the second titration in the presence of sodium fluoride. In the latter case only the free acid is taken into account, since sodium fluoride binds the aluminum, contained in the solution, into the complex, Na_3AlF_6. The aluminum content was calculated by the difference of the total acidity and the free acid content of the solution.

Treatment of the samples with HCl solution and calcination was carried out alternately 5 times.

TABLE 3

Change of Values of Exchange Acidity of Samples of Aluminum Silica Gel as the Result of Alternate Treatment with 1N Solution of Hydrochloric Acid and Calcining (in m-equiv/100 g).

Sample of aluminosilicate	Property	Initial	Order of treatment				
			1	2	3	4	5
Activated bentonite	Exchange acidity	8.4	10.8	10.8	10.8	10.8	11.4
	Content of aluminum in NaCl extract	8.4	10.8	10.8	10.8	10.5	10.8
Alumino-silica gel	Exchange acidity	8.8	4.9	3.7	3.7	2.7	2.1
	Content of aluminum in NaCl-extract	8.8	4.3	2.2	1.9	1.2	0.9
Synthetic alumino-silicate	Exchange acidity	17.0	14.4	10.8	7.8	8.2	7.6
	Content of aluminum in NaCl-extract	17.0	14.4	10.2	7.2	7.6	6.4

Note: The exchange acidity was determined by treatment of the samples with N solution of sodium chloride during a period of one day.

The experiments showed that after each cycle of treatment the exchange acidity of the alumino-silica gel continuously decreased. This depended on the fact that the Si—O—Al bond in alumino-silica gel occurs on its surface, and is easily attacked by acid, which explained the removal from the sample of all the chemically absorbed aluminum.

Calcination of the sample is accompanied by interaction of the remaining free aluminum oxide with the OH groups forming, which, as shown by a specially conducted experiment, led to some increase of the exchange acidity, as a result of the fact that the hydrogen ions were replaced by the more mobile aluminum ions. For example, the exchange acidity of alumino-silica gel, directly after acid treatment, amounted to 3.7 m equiv/100 g, and after calcination —4.9 m equiv/100 g.

The oxide aluminum, replacing the hydrogen ion of the silica gel hydroxyl group, becomes susceptible to removal by subsequent acid treatment. Thus, alternate calcination and acid treatment of alumino-silica gel led to the fact that, after the 5th cycle of treatment, all the aluminum from the sample was removed, and the magnitude of the exchange acidity became negligible.

For activated bentonite, acid treatment did not decrease the magnitude of the exchange acidity, since the montmorillonite structure made the Si—O—Al bond inaccessible to the action of acid. Synthetic alumino-silicate occupied, according to the change of the magnitude of exchange acidity, a position intermediate between activated bentonite and alumino-silica gel, after the 5th cycle of treatment, its exchange acidity had decreased by half. This fact may serve as confirmation of the previously discussed assumption [10] relative to the fact that, into the composition of synthetic aluminosilicate two compounds enter: one — a montmorillonite type, the other — an alumino-silica gel type.

The acid extracted, from synthetic aluminosilicate, all of the aluminum which was bound to the silica gel structure, and the remaining exchange acidity of the sample depended exclusively on the presence of free aluminum oxide in it and on a structure of the montmorillonite type, producing a Si—O—Al bond which was inaccessible to the action of acid.

The calcination of the sample was accompanied by an increase of its exchange acidity, as a result of the fact that the interaction of aluminum oxide with the silica gel hydroxyl group part of the aluminosilicate, led to replacement of the hydrogen ions by the more mobile aluminum ions.

Increase of the exchange acidity of aluminosilicate during the process of replacement of the exchange ions of hydrogen by aluminum ions is illustrated by the data of Table 4.

From the data of Table 3 it followed that the decrease of the exchange acidity of synthetic aluminosilicate ceased, beginning with the 3rd cycle of treatment. This indicates that complete removal of free aluminum oxide was attained in the first two cycles of operation, and the sample lost its capacity to reduce that part of the acidity which depended on its silica gel structure.

Thus, the experimental results led to the conclusion that, in synthetic aluminosilicate, replacement of the exchange ions of hydrogen by Al^- ion occurs because of aluminum entering into the montmorillonite type of structure, and also because of free aluminum oxide, if it was not removed completely from the sample.

TABLE 4

Variation of the Exchange Acidity of Synthetic Aluminosilicate During the Process of Replacement of Exchanged Ions of Hydrogen by Aluminum Ions (5 g sample was shaken for 15 minutes with 60 ml of 1 N solution of NaCl) (in m equiv/100 g)

When salt solution treatment was carried out	Total acidity of solution after treatment of sample with 60 ml of NaCl solution	Aluminum content in NaCl-extract
Immediately after washing off acid	5.83	1.37
After 1 hour	6.05	2.88
After 2 hours	6.05	3.46
After 3 hours	6.34	4.46
After 1 day	7.06	6.48
After 2 days	7.27	6.98
After drying	7.63	7.34
After calcining	7.92	7.63

Note: In the second column of the table are presented values, not of the exchange acidity, but of quantities characterizing its magnitude.

SUMMARY

1. Treatment of silica gel and activated aluminum oxide with a 1 N solution of HCl is accompanied by removal of all the chemically combined aluminum. The OH groups forming interact with the remaining aluminum oxide, as a result of which the hydrogen ions of the active hydroxyl groups are replaced by aluminum. In synthetic aluminosilicate the replacement of exchanged hydrogen ions by aluminum occurs because of aluminum oxide and because of the aluminum entering into the montmorillonite type of structure.

2. The value of the hydrolytic acidity of synthetic aluminosilicate and alumino-silica-gel, determined by treatment with a solution of sodium acetate, exceeded the actual magnitude of the hydrolytic acidity of the samples. This circumstance depended, obviously, on the fact that in the described samples, basic aluminum was found in the absorbed condition, which, being connected with the small activity centers of silica gel, promoted displacement in sodium acetate solution, since the basic form of aluminum, in contrast to trivalent aluminum, was attached to silica gel only by one or two valence bonds.

3. The nature of the variation of the exchange acidity of activated bentonite, synthetic alumino-silicate and silica gel and activated aluminum oxide, which takes place as a result of treatment of samples with hydrochloric acid, may serve as confirmation of the earlier proposal [10] relative to the fact that into the composition of synthetic aluminosilicate, two compounds enter: one – a montmorillonite type, the other – an alumino-silica gel type.

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ION EXCHANGE IN WATER-ORGANIC SOLUTIONS

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By the process of ion exchange, in a narrow sense, is meant exchange reactions between solution and solid phase, as a result of which ions of definite sign are transferred from the liquid phase to the absorbent, returning an equivalent quantity of different ions to the solution. This reaction is the basis of many laboratory and industrial processes in which synthetic ion exchange resins are used.

The ion exchange phenomenon has been the subject of numerous investigations, in which the leading role belongs to Soviet scientists (K. K. Gedroits, E. N. Gapon, B. P. Nikolsky), who formulated strict quantitative theories of these processes.

Ion exchange is widely used for the analytical purposes of separating and purifying aqueous solutions. There have also been attempts to use exchange processes in non-aqueous and mixed solutions. For example, ion exchange is used for purification of acetone from acid and alkali, for removing calcium and magnesium from kerosene, for dry purification of alcohol, glycerin, ethylene glycol, etc.. However, the phenomenon of ion exchange in non-aqueous and mixed solvents has been insufficiently investigated, which seems to be a deterrent to universal use of ion exchange resins in organic and water-organic media.

Theoretically, ion exchange processes are of interest in the investigation of exchanges involving replacement of water in solution by organic solvents. Such a replacement should lead to a change of ionic distribution between solid phase and solution because of property changes of the ions (hydration, interaction with other ions and solvent) and because of property changes of solid absorbent (swelling).

Wiegner [1], who studied ion exchange in permutite in alcohol-water solutions, attempted to account for the effect of media on exchange reactions. She considered the absorbent as a colloidal system, the particles of which carry a negative charge. Ions entering such a system should be stronger the more dehydrated the ions entering the absorbent and the more hydrated the ions entering the solution. Weigner investigated the entrance of Na^+, K^+ and Cs^+ ions into Ca^{++}-permutite and showed that the ionic hydration value decreased with an increase of the per cent of ethyl alcohol in the alcohol-water solutions. The real ionic radii began to play an essential role in exchange, and the order of arrangement of the ions in the lyotropic series changed. Wiegner, assuming that the change of the magnitudes of the cations entering was proportional to the quantity of alcohol in solution, calculated their magnitudes, and they agreed well with experimental data. Weigner also observed a linear relationship between the quantity of ions absorbed and the alcohol concentration. Ion exchange in soils in alcohol-water solutions was studied by Prianishnikov [2], and led to a conclusion similar to that of Wiegner.

Of interest, from the point of view of solvents in cationic exchange processes in silicate systems, is the work of Izmailov and Frantsevich-Zabludovskaya [3], who studied the behavior of the glass electrode in alcohol-water solutions. These authors concluded that a change of the exchange constants of the glass during transition from one medium to another depends only on the change of the ratios of the ionic activities in these solutions, which are numerically equal to:

$$\frac{K_I}{K_{II}} = \left(\frac{a_{H^+}}{a_{Na^+}}\right)_I : \left(\frac{a_{H^+}}{a_{Na^+}}\right)_{II} .$$

where K_I and K_{II} are the exchange constants in media I and II,, a_i is the corresponding activity of an ion in the solutions.

With ion exchange resins, cation exchange in water-organic media was studied by Kressman and Kitchener [4]. The authors found a whole series of experimental facts, the majority of which were not elucidated. The most essential result of the work seems to be the following: 1) the quantity of absorbed alkali ions increased with an increase in the concentration of the organic solvent, and 2) in alcohol-water solutions the logarithm of the exchange constant changed linearly with the change of alcohol concentration; in acetone-water solutions the magnitude of the constant appears to be a linear function of the acetone concentration. In particular, for exchange of different

TABLE 1

Ionic Exchange of Barium and Sodium on Vofatit C in Aqueous Solutions

Expt. No.	Volume ratio of discharged solutions (V_{Ba}:V_{Na})	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K_{exptl.}$
		C_{Ba}	C_{Na}	G_{Ba}	G_{Na}	
			Na-Vofatit			
1	3 : 1	0.05103	0.02398	3.04	0.0465	3.98
2				3.03	0.0561	3.29
3	1 : 1	0.03571	0.04928	2.95	0.121	3.70
4				2.96	0.126	3.52
5	1 : 3	0.01754	0.07476	2.79	0.256	3.69
6				2.81	0.257	3.69
7	1 : 5	0.01206	0.08023	2.73	0.347	3.48
8				2.73	0.340	3.53
9	1 : 10	0.006117	0.09032	2.56	0.501	3.68
10				2.58	0.512	3.62
				Average		3.62 ± 0.13
			Ba-Vofatit			
11	1 : 10	0.006117	0.09032	2.58	0.519	3.58
12				2.57	0.520	3.53
13	1 : 40	0.001630	0.09758	2.10	0.961	3.65
				Average		3.59 ± 0.04

ions in water-organic solvents the authors explained the effect of solvents on the basis of effective ionic diameters, according to Debye ($\underline{a}^0$).

Thus, the reports in the literature on ion exchange in non-aqueous and mixed solutions do not give a complete picture of the mechanism of the exchange processes in such media. The difficultly of interpretation of the results obtained in water-organic solutions is accounted for by the meagerness of information on the activity of salts in the presence of non-aqueous solvents.

In the present report cation exchange, with ion exchange resins under dynamic conditions in alcohol-water and acetone-water solutions, was studied for the purpose of examining the applicability of the exchange laws to ion exchange processes in water-organic media, and also to analyses of the operation of a column in such solutions.

EXPERIMENTAL

1. Equilibrium Established During Cation Exchange in Water-Organic Solutions

a) Ion exchange of sodium and barium in alcohol-water solutions. Vofatit C (carboxyl ion exchange) was used as an absorbent for investigating ion exchange in alcohol-water solutions. Barium and sodium served as the exchanging ions. Experiments were carried out principally on the sodium form of Vofatit C, which was obtained by treatment of the initial absorbent with 0.5 N NaCl. Part of the experiment was carried out on the barium form of Vofatit C. The ionic strength of the solutions was kept constant and equal to 0.1. The operating solutions were prepared from 0.0667 N barium chloride solution and 0.1 N sodium chloride solution in the ratios: 3:1, 1:1, 1:3, 1:5, 1:10 and 1:40. The solutions contained 0, 15.5, 30, 50 and 71 weight per cent of ethyl alcohol. The equilibrium ionic concentrations were determined by gravimetric methods: barium as the sulfate and sodium as sodium-zinc uranylacetate. The pH of the active solutions was 6.15-6.40.

The method of conducting the experiments consisted of the following: Into a small weighed column with perforated bottom was placed a weighed portion of cationite (0.3-0.4 g), which was brought into equilibrium with

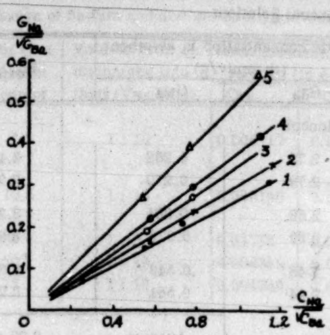

Fig. 1. Isotherms of ionic exchange of sodium and barium for Vofatit C in aqueous and alcoholic-aqueous solutions. 1) 0% C_2H_5OH; 2) 15.5% C_2H_5OH; 3) 30% C_2H_5OH; 4) 50% C_2H_5OH; 5) 71% C_2H_5OH.

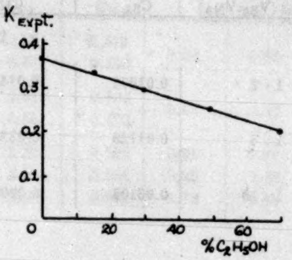

Fig. 2. Relationship of experimental ionic exchange constant of sodium and barium to the per cent content of alcohol in solution.

solutions of barium and sodium ions, taken in different proportions. For this purpose solution was supplied to the column at a rate of 15-20 ml/hr from a bottle with attached tube. Each weighed portion of absorbent was treated with 1 liter of solution. After completion of the operation, the excess of solution was carefully drawn off, and the column was weighed in order to determine the amount of mechanically retained solution, for which a correction was introduced for swelling of the cationite. Then the cationite was washed with 150-200 ml of 0.1 N HCl solution until the absorbed ions were completely displaced. Sodium and barium ions were determined quantitatively in the hydrochloric acid solution obtained. The experimental data served for calculation of the exchange constant, which was calculated from the Nikolsky [5] equation:

$$K = \frac{C_{Na}}{\sqrt{C_{Ba}}} \frac{\sqrt{G_{Ba}}}{G_{Na}}, \tag{1}$$

where C_i is the concentration of an ion in the equilibrium solution (in m equiv/g), G_i is the quantity of absorbed ion (in m equiv/g), K is the exchange constant.

The experimental results for the aqueous solutions are presented in Table 1.

Experiments 1-10 were carried out on the sodium form of Vofatit, and 11-13 — on the barium form, the latter for the purpose of verification of the reversibility of the process. Comparing the exchange constants for experiments on sodium and barium cationites, it is possible to draw conclusions concerning the complete reversibility of the ion exchange of barium and sodium on Vofatit C in aqueous solution.

In Table 2 experimental results for exchange of the same cations in alcohol-water solutions are presented. In Fig. 1 exchange isotherms of sodium and barium on Vofatit C in water and alcohol solutions are represented. From this figure it is seen that the experimental points for all the concentrations of alcohol studied lie on a straight line passing through the origin of the coordinates, and consequently, the cation exchange in synthetic resin absorbent both in aqueous and alcohol solution obeyed equation (1). From Tables 1 and 2 it follows that the exchange constant (will be designated by $K_{exptl.}$) for sodium Vofatit, calculated from equation (1), appears to be a function of the per cent alcohol content of the solution. The graphical relationship of $K_{exptl.}$ to the per cent content of alcohol is shown in Fig. 2.

Results of the experiments on barium Vofatit are collected in Table 3. From these data a conclusion can be drawn concerning a certain irreversibility of the process of ion exchange in alcoholic solution ($K'_{exptl.}$ — the exchange constant for barium Vofatit). An elucidation of these phenomena will be given below.

TABLE 2

Ion Exchange of Barium and Sodium on Vofatit C in Alcohol-Aqueous Solutions

Expt. No.	Volume ratio of discharge solutions ($V_{Ba}:V_{Na}$)	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K_{exptl.}$
		C_{Ba}	C_{Na}	G_{Ba}	G_{Na}	
			15.5% Ethyl Alcohol			
1	1 : 3	0.01673	0.07495	2.78	0.262	3.41
2				2.79	0.270	3.37
3	1 : 5	0.01123	0.08338	2.68	0.384	3.36
4				2.69	0.376	3.36
5	1 : 10	0.06105	0.09087	2.48	0.549	3.33
6				2.44	0.561	3.25
					Average	3.37 ± 0.06
			30% Ethyl Alcohol			
7	1 : 3	0.01718	0.07440	2.78	0.298	3.01
8				2.74	0.293	3.04
9	1 : 5	0.01130	0.08321	2.63	0.442	2.87
					Average	2.97 ± 0.07
			50% Ethyl Alcohol			
10	1 : 3	0.01671	0.07443	2.69	0.367	2.57
11				2.68	0.372	2.54
12	1 : 5	0.01170	0.08420	2.59	0.479	2.62
13				2.39	0.477	2.62
14	1 : 10	0.00638	0.09022	2.36	0.646	2.68
15				2.37	0.641	2.69
					Average	2.62 ± 0.04
			71% Ethyl Alcohol			
16	1 : 3	0.01774	0.07317	2.60	0.419	2.11
17				2.62	0.411	2.16
18	1 : 5	0.01137	0.08214	2.48	0.605	2.01
19				2.42	0.614	1.95
20	1 : 10	0.00656	0.08929	2.23	0.840	1.97
21				2.24	0.830	1.99
					Average	2.03 ± 0.07

b) Ion exchange of sodium and ammonium in acetone-water solutions. In this part of the work, the cationic exchange equilibrium in acetone-water solutions was studied. The exchange constant was calculated from the equation

$$K = \frac{G_{Na}\,C_{NH_4}}{G_{NH_4}\,C_{Na}}\,. \tag{2}$$

The method of operation was analogous to the preceding. A sample of domestic sulfo-cationite SBS was used as the cationite. Into the column was placed 1 g of SBS resin, which was saturated with ammonium ion, and through

TABLE 3

Ion Exchange of Barium and Sodium on Barium Vofatit in Aqueous and Alcohol-Water Solutions

Expt. No.	Per cent alcohol content	Volume ratio of discharged solutions ($V_{Ba}:V_{Na}$)	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K'_{exptl.}$	$K_{exptl.}$	ΔK
			C_{Ba}	C_{Na}	G_{Ba}	G_{Na}			
1	0	1 : 10	0.006117	0.09032	2.58	0.519	3.59	3.62	−0.03
2					2.57	0.520			
3	15.5	1 : 10	0.006105	0.09087	2.56	0.503	3.68	3.37	0.31
4					2.56	0.503			
5	30	1 : 3	0.01718	0.07490	2.79	0.293	3.06	2.97	0.09
6	50	1 : 10	0.006382	0.09022	2.57	0.558	3.25	2.62	0.63
7	71	1 : 10	0.006390	0.09103	2.57	0.661	2.76	2.03	0.73

TABLE 4

Ionic Exchange of Sodium and Ammonium in Aqueous Solutions

Expt. No.	Volume ratio of discharged solutions ($V_{Na}:V_{NH_4}$)	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K_{exptl.}$
		C_{Na}	C_{NH_4}	G_{Na}	G_{NH_4}	
				NH_4-Cationite		
1	1 : 3	0.02506	0.07489	0.408	1.99	0.612
2				0.413	2.00	0.616
3	1 : 1	0.04996	0.04953	0.839	1.49	0.558
4				0.839	1.49	0.553
5	3 : 1	0.07435	0.02491	1.46	0.908	0.538
6				1.46	0.91	0.539
				Na-Cationite		
7	1 : 3	0.02500	0.07573	0.410	1.99	0.623
8				0.411	1.99	0.623
9	1 : 1	0.05014	0.05054	0.830	1.49	0.561
10				0.833	1.49	0.564

which was passed a mixture of sodium chloride and ammonium chloride solutions, taken in different ratios (1:3, 3:1, and 1:1). The ionic strength was kept constant and equal to 0.1. The solutions were passed through the column at a rate of 1 ml/min until equilibrium was established. After washing with aqueous solution, the absorbed ions retained in the column were displaced by 0.1 N hydrochloric acid. In the filtrate ammonia was determined by distillation, sodium – by a gravimetric method using zinc uranylacetate. The results of the experiments on the ion exchange of sodium and ammonium in aqueous solutions are presented in Table 4.

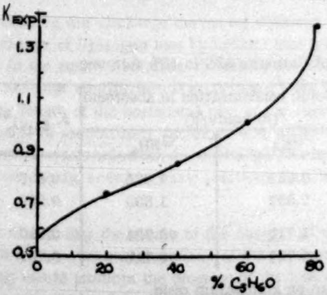

Fig. 3. Relationship of the experimental ionic exchange constant for ammonium and sodium to the percent content of acetone in the solutions.

The results of Table 4 indicate a regular "rate" of the exchange constant for a change of the solution composition. This phenomenon was observed in a series of cases of ion exchange on resins [6] and, apparently, may be explained by the change of the activity coefficients of the ions in the solid phase. The process of cation exchange of sodium and ammonium in aqueous media seems to be reversible, which can be

TABLE 5

Ion Exchange of Sodium and Ammonium in Acetone-Water Solutions with Cationite SBS

Expt. No.	Volume ratio of discharged solution (V_{Na}:V_{NH_4})	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K_{exptl.}$
		C_{Na}	C_{NH_4}	G_{Na}	G_{NH_4}	
20% Acetone						
1	1 : 3	0.02503	0.07494	0.484	1.864	0.774
2				0.492	1.872	0.790
3	1 : 1	0.04997	0.04998	1.014	1.369	0.733
4				1.001	1.362	0.738
5	3 : 1	0.07509	0.02499	1.586	0.761	0.694
6				1.575	0.766	0.682
40% Acetone						
7	1 : 3	0.02540	0.07492	0.570	1.860	0.904
8				0.559	1.849	0.892
9	1 : 1	0.05171	0.05008	1.120	1.291	0.843
10				1.119	1.285	0.846
11	3 : 1	0.07155	0.02407	1.720	0.718	0.801
12				1.730	0.718	0.800
60% Acetone						
13	1 : 3	0.02531	0.07637	0.616	1.744	1.070
14				0.614	1.733	1.070
15	1 : 1	0.05062	0.04982	1.194	1.185	0.991
16				1.214	1.190	1.000
17	3 : 1	0.07318	0.02454	1.761	0.605	0.975
18				1.762	0.610	0.970
80% Acetone						
19	1 : 3	0.02495	0.07491	0.827	1.038	1.517
20				0.824	1.651	1.499
21	1 : 1	0.04997	0.04960	1.419	1.010	1.388
22				1.394	1.015	1.363
23	3 : 1	0.07440	0.02480	1.940	0.505	1.275
24				1.932	0.510	1.263

TABLE 6

Ion Exchange of Sodium and Ammonium on the Sodium Form of Cationite SBS in 40% Acetone

Expt. No.	Volume ratio of discharged solution (V_{Na}:V_{NH_4})	Ionic concentration in solution (m equiv/g)		Ionic concentration in absorbent (m equiv/g)		$K'_{exptl.}$**	$K_{exptl.}$*
		C_{Na}	C_{NH_4}	G_{Na}	G_{NH_4}		
1	1 : 3	0.02513	0.07504	0.552	1.835	0.899	0.898
2				0.552	1.830	0.900	
3	3 : 1	0.07484	0.02505	1.710	0.724	0.790	0.800
4				1.714	0.719	0.797	

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* $K_{exptl.}$ — the ion exchange constant of sodium and ammonium on ammonium resin.

** $K'_{exptl.}$ — the ion exchange constant of sodium and ammonium on sodium resin.

seen from the results of Table 4, comparing the exchange constants for ammonium and sodium resins with similar ratios of ionic concentrations of sodium and ammonium in solution.

In the acetone-water solutions the experiments were carried out with the same ionic ratios and the same ionic strength as were used in the aqueous solutions. The concentrations of acetone in the solutions amounted to 20, 40, 60, 80 weight per cent. Results of the experiments on ion exchange of ammonium and sodium in different acetone-water solutions are presented in Table 5, which shows that for all acetone-water solutions, as also for the aqueous solutions, a "rate" exchange constant for change of the concentration ratios of ammonium and sodium in solution is observed. If one compares the magnitudes of the exchange constants in different acetone-water solutions (Fig. 3) then it can be seen that for increases of the acetone content in solution the exchange constant increases.

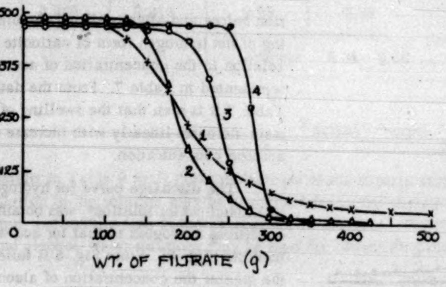

Fig. 4. Discharge curves of the exchange of hydrogen ion for sodium in cationite SBS in different acetone-water solutions. Acetone (in %): 1) 0; 2) 20; 3) 40; 4) 60.

As seen from the data of Table 5, subsequent addition of acetone promotes the absorption of sodium ion and decreases the absorption of ammonium ion.

In order to elucidate the reversibility of the exchange process in acetone-water medium, experiments were made using the sodium form of SBS Resin in a 40% solution of acetone. Results of these experiments are presented in Table 6.

A direct comparison of the exchange constant with the reverse reaction shows that the ion exchange process of sodium and ammonium in acetone-water solutions appears to be completely reversible.

2. Ion Exchange in Water-Organic Solutions Under Dynamic Conditions

Study of the cation exchange in acetone-water and alcohol-water solutions under dynamic conditions was carried out, using the method of discharge curves. The discharge curves, as is well-known, express the relationship of the concentration of the discharging solution to the volume (weight) of the liquid flowing through the column. The method of discharge curves permits the determination of the relative exchange rate, the dynamic exchange capacity and the character of the distribution of ions in the column.

To obtain the discharge curves, the following experiments were planned. A weighed portion of cationite (5-6 g) in the hydrogen form was placed in the column and moistened with the corresponding solvent. A solution of 0.05 N NaCl was passed through the column at a constant rate (1 ml/min). The filtrate was collected in a separate flask. The total fraction of the filtrate amounted to 20-25 g. In each fraction the concentration of the displaced ions was determined.

The results obtained are represented in Fig. 4 in the form of discharge curves, expressing the relation of the hydrogen ion concentration in the displacing solution to the amount of filtrate in grams.

Comparing the discharge curves for different acetone-water solutions, it is possible to point out that the rate of ion exchange of hydrogen ions by sodium ions increases with increase of the per cent content of acetone in the solution. In the aqueous solutions the discharge curves have a more sloping character than in the mixed solutions, i.e., the exchange equilibrium is established more rapidly in the acetone-water solutions than in the aqueous solutions. The length of the horizontal part of the curve, corresponding to a constant concentration of hydrogen ions (until passage of sodium ion), increases with an increase of the acetone concentration in the solution. Consequently, in the acetone-water solutions the exchange proceeds more rapidly than in aqueous solutions; and for the same rate of filtration, for the acetone-water solutions the filtrate may be recovered more completely than for the aqueous solutions.

For elucidating the nature of the changes of the discharge curves with subsequent replacement of water in the mixed solvent by acetone, the effect of the solvents on the swelling of the SBS cationite was investigated. Increase of swelling should promote the progress of the ions into the absorbent and, consequently, should increase the exchange rate. The magnitude of swelling of cationite SBS was determined by a comparison of the volume or weight of solu-

TABLE 7

Relation of Swelling of Cationite SBS to the Concentration of Acetone

Percent content of acetone	Quantity (in g) of absorbed solution per 1 g of resin
0	1.60
20	1.74
40	1.84
60	1.94
80	2.06

TABLE 8

Relation of Swelling of Cationite SBS to the Concentration of Alcohol

Percent content of alcohol	Quantity (in g) of the absorbed solution per 1 g of resin
0	0.667
28	0.824
60	0.995
80	1.092

tion before and after swelling. Results of swelling of the hydrogen form of cationite SBS in relation to the concentration of acetone are represented in Table 7. From the data of Table 7 it is seen that the swelling of the SBS resin increases linearly with increase of the acetone concentration.

The discharge curve for hydrogen ions in alcohol-water solution* was obtained under conditions analogous to that for acetone-water medium (Fig. 5). From Fig. 5 it follows that, the greater the concentration of alcohol in the solution, the later the passage of the absorbed ion (sodium) occurs, i.e., the longer the horizontal part of the line, and the steeper the discharge curves. Similarly, acetone-water solutions, to the extent of the increase of the alcohol concentration in mixed solvent, increase the rate of ion exchange.

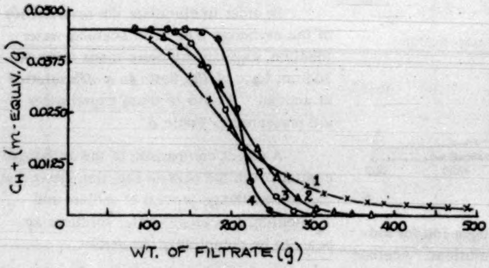

Fig. 5. Discharge curves of hydrogen ion exchange for sodium ion in cationite SBS in different alcohol-water solutions. Alcohol (%): 1) 0; 2) 28; 3) 60; 4) 80.

In direct relation to the increase of the rate of exchange in alcohol-water solutions is the increase of swelling capacity of the SBS resin in mixed solutions, with an increase of alcohol concentration. Results of the swelling of the hydrogen form of the SBS resin in alcohol-water solutions of 0.05 N sodium chloride are presented in Table 8.

DISCUSSION OF RESULTS

Results of the experiments on the ion exchange of barium and sodium in alcohol-water solutions on Vofatit C (Fig. 2) showed that, on replacement of water in the mixed solvent by alcohol, the exchange constant calculated from the Nikolsky Equation decreased with an increase of the alcohol content. In order to account for this fact, it is simple to assume that the change depends on the change of the activity coefficients of the ions in the solution, with an increase of the alcohol content. For verification of this assumption it is necessary to calculate the actual exchange constant, i.e., the value of the constant, expressed by the activity of the ions. Results of such a calculation are presented in Table 9. The ionic activity coefficients of barium and sodium in alcohol-water solutions were calculated from the Vinogradov [7]** nomogram, based on the use of the first approximation of the Debye and Hückel equation.

The actual exchange constant was calculated from the equation

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* In these experiments, S. B. Evinina participated.

** Calculation of the activity coefficient values seems to be an approximation, since on the nomogram the individualities of the single ions were not studied, but, in spite of the inaccuracy of the absolute values of the activity coefficients, the character of their changes with decrease of the dielectric constant of the media corresponds to reality.

TABLE 9

Experimental and Actual Values of the Exchange Constant for Different Alcohol-Water Solutions

Percent alcohol content	γ_{Ba}	γ_{Na}	$K_{exptl.}$	K_{actual}
0	0.240	0.705	3.62	5.20
15.5	0.178	0.649	3.38	5.21
30.0	0.100	0.574	2.97	5.39
50.0	0.055	0.490	2.60	5.37
71.0	0.020	0.373	2.03	5.36
			Average	5.31 ± 0.08

TABLE 10

Experimental and Actual Values of the Exchange Constant for Different Acetone-Water Solutions

Percent acetone content	γ_{Na}	γ_{NH_4}	$K_{exptl.}$	K_{actual}
0	0.82	0.75	0.61	0.56
20	0.80	0.68	0.78	0.66
40	0.75	0.60	0.90	0.73
60	0.66	0.47	1.07	0.76

$$K_{actual} = K_{exptl.} \frac{\gamma_{Na}}{\sqrt{\gamma_{Ba}}} . \qquad (3)$$

Results in Table 9 show that the decrease of the experimental exchange constant with increase of the alcohol concentration in the solution may be accounted for by the change of the relation of the activity coefficients of the barium and sodium ions in the alcohol-water solutions. The stability of the actual exchange constant in the water and alcohol-water solutions may be used for determining the ratio of the activity coefficients

$$\gamma_{M_1}^{1/z_1} : \gamma_{M_2}^{1/z_2} .$$

To account for the anomalous behavior of barium Vofatit (Table 3), it is interesting to follow the relation of the absorption capacity of sodium and barium to the concentration of alcohol in the solution. This relationship is represented graphically in Fig. 6, constructed from the data of Tables 1 and 2.

From Fig. 6 it is seen that for sodium Vofatit (continuous curve), with an increase of the quantity of alcohol, G_{Na} increases, but G_{Ba} decreases. For barium Vofatit (dotted curve) something peculiar takes place, explained apparently, by the irreversibility of the exchange process in alcohol-water solutions. The entering of barium ion into the barium Vofatit does not depend on the alcohol concentration, but remains equal to the magnitude of G_{Ba} for the aqueous solution. Such a result was obtained for all concentrations studied.

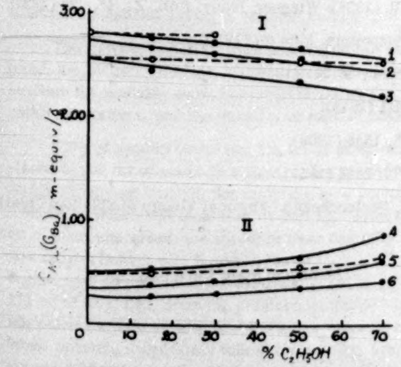

Fig. 6. Relation of G_{Na} and G_{Ba} to the per cent content of alcohol for sodium and barium Vofatit. I) G_{Ba} = f (% C_2H_5OH); II) G_{Na} = f (% C_2H_5OH). 1) C_{Ba} = 0.0175; 2) C_{Ba} = 0.0120; 3) C_{Ba} = 0.0016; 4) C_{Na} = 0.090; 5) C_{Na} = = 0.083; 6) C_{Na} = 0.075.

The experimental results obtained in the acetone-water solutions (Tables 4, 5, 6 and Fig. 3) showed that, for an increase of the acetone concentration, the value of the exchange constant calculated from Equation (2) increased, since for an increase of the per cent of acetone in the solution, the quantity of absorbed sodium ion increases and the quantity of absorbed ammonium ion decreases. On the part of the curve (Fig. 3) up to an acetone content equal to 60%, $K_{exptl.}$ depends linearly on the acetone concentration. For concentrations of acetone exceeding 60% the curve rises sharply. To account for variance of the exchange constant with an increase of the acetone concentration, the "actual" exchange constant expressed by the activity of the ammonium and sodium ions in the mixed solutions was calculated, just as for the alcohol-water solutions. The activity coefficients in the acetone-water solutions were evaluated from the Vinogradov [7] nomogram. Results of the calculation of the "actual" exchange constants are presented in Table 10.* The calculation is of an extremely approximate character.

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* $K_{exptl.}$ was given for a concentration ratio of sodium and ammonium ions in solution, equal to 1:3.

However, a comparison of the experimental and "actual" constants showed that the "actual" exchange constant has a smaller rate than does the experimental constant during transition from aqueous to acetone-water solutions.

The experimental material on cation exchange in water-organic solutions, under dynamic conditions, leads to the conclusion that the rate of the process increases substantially with an increase of the concentration of the organic component in solution. If one compares the discharge curves for different acetone-water and alcohol-water solutions (Figs. 4 and 5), it is easy to see that the initial sloping of the curves from the horizontal, corresponding to the moment of appearance of sodium ion in the filtrate (passage),* occurs earlier in the aqueous solutions and later in the solutions having the largest content of organic component. The effect of the organic component on the kinetics of the ion exchange processes is found to be in direct relation to the change of the swelling capacity of the absorbent.

The results may be of essential practical value for selection of the most favorable conditions of separating and concentrating cations with the help of ion exchange under dynamic conditions.

The authors are deeply grateful to Professor B. P. Nikolsky for valuable direction during performance of this work.

SUMMARY

1. The process of ion exchange in alcohol-water and acetone-water solutions was studied.

The applicability of the Nikolsky isotherm equation to the exchange process in water-organic solutions was shown.

2. The relationship of the cations entering the absorbent to the quantity of organic component in solution was studied. An increase of the alcohol content facilitated the absorption of sodium ion and hindered the absorption of barium ion by Vofatit C. Increase of the acetone content promoted the absorption of the sodium ion and decreased the absorption of the ammonium ion by SBS resin.

3. The process of ion exchange was investigated under dynamic conditions in aqueous and water-organic solutions. It was shown that in water-organic medium the exchange process proceeds with a greater rate than in water, in which the rate increased with increase of the content of organic substance in solution.

4. The swelling capacity of cationite SBS in relation to the composition of the solution was determined. It showed that swelling increased linearly with an increase of the content of organic component in solution (acetone or alcohol).

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* Appearance of sodium ion in the filtrate was controlled by qualitative test.

HETEROTRIACIDS

I. PHOSPHOMOLYBDENOVANADIC AND PHOSPHOTUNGSTOVANADIC ACIDS

A. I. Kokorin

A comparatively large number of investigations have been devoted to the synthesis of heteropolydiacids and their derivatives. The work of Nikitina and co-workers [1] on the synthesis of phosphomolybdic, phosphotungstic, silicomolybdic and silicotungstic acids, by the ester method, has been particularly fruitful. On the subject of separating the heterotriacids quantitatively in the free state, the work published in the literature is extremely limited. The work of Ivanov-Emin [2] on the synthesis of germanicmolybdenovanadic acid, also by the ester method, is of great interest in this respect. For the sake of brevity, we call the heteropolytriacids, "heterotriacids".

A considerably larger number of papers has been published on the synthesis of heterotriacid sals salts by the crystallization method; however, isolation of the acids in the free state by this method involves considerable technical difficulties and the expenditure of large quantities of reactants.

Davidov and Vaisberg very effectively applied the formation in solution of the phosphotungstovanadic complex to the photocolorimetric determination of vanadium [4]. One of the phosphorous determinations also is based on a reaction forming the phosphomolybdenovanadic complex [5].

Some of the heterotriacids forming in solution are used as analytical reagents, for example for determining antimony and thallium phosphotungstomolybdic reagent is used [6]. However, the use of reagents which are mixtures of the complex compounds forming in solution in indefinite quantity, with an excess of the initial substances and other products of reaction, often does not give reproducible results in quantitative analysis.

Consequently, the separation of the heterotriacids in the free state, and a study of their properties is of definite interest.

In the present report we present results of the synthesis, by the ester method, of phosphomolybdenovanadic and phosphotungstovanadic acids, and determinations of their compositions in the free state.

Phosphomolybdenovanadic Acid

Synthesis. In order to obtain this acid in the free state, we first* used a method proposed by Nikitina for synthesis of phosphomolybdic acid [1]. As shown by further investigations, the phosphomolybdenovanadic acid precipitating in the free state (under the conditions of synthesis of phosphomolybdic acid) belongs to the class of unsaturated compounds having a variable composition.

The starting materials used in the synthesis of phosphomolybdenovanadic acid, in the method that we proposed, are sodium vanadate, phosphoric acid and molybdic acid. The quantity of starting materials was calculated from the probable formula $-H_7[P(Mo_2O_7)_5V_2O_6]$. The phosphoric and molybdic acids were used in stoichiometric proportions, and the quantity of sodium vanadate used was in 2 and 3-fold excess.

7.5 g of sodium vanadate, 1.2 ml of phosphoric acid (d 1.44) and 18.5 g of crystalline molybdic acid were placed in 200 ml of water in a flask with a ground-in reflux condenser,and boiled for a period of 2 hours; thus, during 15 minutes boiling, the molybdic acid completely dissolved, and the solution acquired a cherry color, the intensity of which was increased by boiling. After cooling, the solution was transferred to a separatory funnel, 50 ml of ether was added, the solutions were carefully mixed, and then 45 ml of concentrated HCl was introduced gradually; a heavy, oily liquid began to form – the ester of the heterotriacid. The concentration of acid at the beginning of formation of the ester was equal to 1.7 N. Further formation of ester ceased after introduction of 110 ml of HCl, i.e., after the acid concentration was 3.3 N. The ester had a dark cherry color; the aqueous layer was colored a pale yellow, and the upper ether layer – an orange color. After settling, the ester layer was transferred to another separatory funnel for washing, into which first were introduced 200 ml of water, 110 ml of hydrochloric acid and several milliliters of ether. After mixing and subsequent settling, the ester was transferred to a small crystallizer, and a small portion of water was added, with stirring, until the ester was completely decomposed and the ether was removed (until cessation of effervescing). The crystallization began at room temperature and continued through several hours (if little water was added). The crystals were ruby-red and had clearly expressed boundaries. In order to separate the crystals, filtration was carried out, under low vacuum, using a glass funnel with quartz plate No. 1. The yield was about 80% of the theoretical. During storage in a dark bottle, the product was stable for a period of many months.

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* K. A. Desyatnik participated in the work.

Analysis. Determinations of the water of crystallization were carried out by drying in a drying chamber at a temperature of 105°, and by the hydride method. The quantity of water of crystallization depends on the conditions of crystallization and does not appear to be constant in the individual syntheses; it fluctuated from 15 to 22%.

In order to determine phosphorus, molybdenum and vanadium, we were successful in finding a reliable and rapid method of analysis, which is described below. As our investigations showed, the cationite — espatite-1, quantitatively sorbs molybdenum, tungsten and vanadium even at relatively high acidity, if the heterotriacid is first decomposed and the elements obtained are reduced to their lowest valence. Determination of phosphorus is easily carried out on the solution after separating molybdenum and vanadium. Determination of molybdenum and vanadium was carried out on a separate portion of a solution of the heterotriacid after decomposition of its complex anion and reduction by zinc amalgam. The absorption was carried out in a tube, 1.5 cm in diameter and 70 cm long, having a glass stopcock, with a column height of espatite of 65 cm.

A weighed portion of about 0.7 g of the sample to be analyzed was dissolved in a measuring flask of 50 ml capacity, from which 5 ml of solution was taken for determination of phosphorus, and the complex anion was decomposed with 5 ml of H_2SO_4 (1:1) by boiling for a period of 1-2 minutes. The solution, after boiling and cooling, had only a yellow tint. After decomposing the complex of the solution in question, it was transferred to a funnel arrangement for reduction, for which 5 ml of water and 4-5 ml of 3% zinc amalgam were introduced [7], then a current of carbon dioxide was passed through the upper stopcock through the semiclosed plug — until the air was displaced from the separatory funnel and then the plug was closed and the separatory funnel was shaken for several minutes. The shaking was carried to the point at which the solution acquired a dark green color (the color of a solution of trivalent molybdenum). The solution, diluted to 100 ml was passed through cationite at a rate of 6-7 ml per minute, and the filtrate was collected in a 250 ml measuring flask. After discharge of the solution, the cationite was washed with water until the measuring flask was filled to the mark.

To 25 ml of the filtrate in order to determine phosphorus, 1 ml of H_2SO_4 (1:1) and 2 ml of concentrated HNO_3 were added and the solution was concentrated until vapors of sulfuric acid appeared, for the purpose of decomposition of the organic substance, recovered from the espatite, which interferes with the determination of phosphorus. Phosphorus was determined photocolorimetrically by the method of A. Ya. Bursuk [8] in the form of the phosphomolybdo complex, with subsequent reduction of the iron salts in the presence of sodium sulfite. For determination of the sum of molybdenum and vanadium, a reduction analogous to that described for the determinationof phosphorus was carried out using zinc amalgam. Later the zinc amalgam was transferred to a vessel, and 10 ml of hot 10% solution of ammonium ferric alum was rapidly introduced into the funnel, in order to oxidize the molybdenum and vanadium. After careful mixing, 5 ml of phosphoric acid was added. The molybdenum, therefore, was oxidized to the hexavalent, and vanadium to the quadrivalent form. The reduced iron and the vanadium were titrated with a 0.05 N solution of potassium permanganate. The number of milliliters of the latter was equivalent to the total contents of molybdenum (III → VI) and vanadium (IV → V).

Determination of vanadium was carried out by a further titration of the solution with Mohr's salt in the presence of phenylanthranilic acid as indicator.

Results of the analyses are presented in Table 1.

TABLE 1

Composition of the Phosphomolybdovanadic Acid Obtained

Sample No.	Composition of the complex						H_2O (%)	Ratios P : Mo : V : H_2O
	P		Mo		V			
	mg	mg-at	mg	mg-at	mg	mg-at		
1	1.02	0.03	27.6	0.29	2.06	0.06	21.85	1 : 9.6 : 2 : 28
2	1.12	0.036	34.2	0.35	3.57	0.07	16.1	1 : 9.8 : 2 : 19
3	1.29	0.042	40.3	0.42	4.08	0.08	20.0	1 : 10 : 1.9 : 15

From the composition of the phosphomolybdovanadic acid it is possible to conclude that, under the described conditions of synthesis, the V_2O_6 radical occupies one coordination site in the complex anion, and small deviations from this condition may be explained as analytical error. Therefore, the compound obtained may be expressed by the formula, $H_7[P(Mo_2O_7)_5V_2O_6] \cdot nH_2O$, where the number of molecules of water, (n), may equal from 15 to 28.

Phosphotungstovanadic Acid

Synthesis. Preparation of this acid under conditions analogous to those for production of phosphomolybdenovanadic acid did not give positive results. This may be explained by the fact that in acid medium a precipitate of tungstic acid forms. The latter only partially enters into reaction with the remaining starting material, and forming in small quantities, the ester of the heterotriacid seems to be contaminated to a high degree. Preliminary conversion of the tungstate to para-tungstate, and use of it for the synthesis, also did not accomplish the purpose. Use of the quantitative proportions of the starting material cited by Gmelin [9] for the synthesis of the ammonium salt of phosphotungstovanadic acid, in preparation of the heterotriacid, leads to formation of the ester, but separation of the crystalline product was not successful, since after removal of ether, a viscous, gummy mass forms. Analysis of the dried product showed that a mixture of compounds of indefinite composition formed. After a series of preliminary experiments* on determination of optimal conditions of the synthesis of phosphotungstovanadic acid we came to the conclusion that, if one starts with 3 times the stoichiometric quantity of vanadium and if the synthesis is carried out with a large excess of phosphoric acid, a heterotriacid of definite composition forms.

Nine grams of Na_2VO_3 was dissolved by heating in 100 ml of water, and simultaneously, 40.6 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 150 ml of water. Into the latter solution were introduced 60 ml of H_3PO_4 (d 1.8) and 5 ml of H_2SO_4 (1:1). The solutions obtained were heated to boiling, decanted together into a flask having a reflux condenser, and the boiling was extended for a period of 1 hour. The solution was dark-red in color. After cooling, it was transferred to a separatory funnel, and 150 ml of ether and, in separate portions of 50 ml, a total of 300 ml H_2SO_4 (1:1), were added. Washing of the ester was accomplished with 9 N H_2SO_4, saturated with ether. After careful settling, the ester was transferred to a small crystallizer, 10 ml of water was added, and the mixture was carefully stirred with a glass stirring rod until the ether was completely removed. Crystallization proceeded at room temperature. Dark red crystals formed and they were separated from the mother solution by filtration through a porous funnel. Phosphotungstovanadic acid is less stable than phosphomolybdenovanadic acid. During storage it becomes difficultly soluble in water in the cold, but dissolves well on heating.

Analysis. Removal of the water of crystallization from this heterotriacid by drying proceeds considerably more difficultly than from the phosphomolybdenovanadic acid, and requires heating to 190°. Since at such a temperature it may decompose, it is more dependable to carry out the determination of the water content by the hydride method.

For determination of phosphorus, tungsten and vandium a weighed portion of about 0.7 g was dissolved in a measuring flask of 50 ml capacity. For the phosphorus determination, 5 ml of the solution obtained was transferred to a funnel for reduction, for which 20 ml of concentrated HCl and 5 ml 3% lead amalgam were added, and with plug open, the funnel and contents were heated over boiling water. After heating to 60-70°, carbon dioxide was passed through the lateral stopcock, with shaking, until the solution acquired a dark yellowish-green color. Tungsten, thus, was reduced to the trivalent, and vanadium to the divalent form. Later more water was added, saturated with carbon dioxide to a total volume of 100 ml, the solution was stirred, and the lead amalgam was transferred to a vessel.

Separation of tungsten and vanadium from phosphorus by means of espatite, and further determination of phosphorus in the filtrate, are carried out also, as for analysis of phosphomolybdenovanadic acid.

In order to determine the sum of tungsten and vanadium, 10 ml of the original phosphotungstovanadic acid solution was placed in a funnel previously prepared for reduction, 40 ml of concentrated HCl and 10 ml of 3% lead amalgam were added, and the reduction carried out. After the reduction, the amalgam was transferred to a vessel and the solution was treated with 40 ml of 0.05 N solution of potassium dichromate. Thus, tungsten was oxidized to the hexavalent state and precipitated as tungstic acid, and vanadium was oxidized to the quadrivalent state. After introduction of ~0.2 g of potassium iodide, the excess dichromate was titrated with a 0.05 N solution of thiosulfate, in the presence of starch, to a blue-green color.

For determination of vanadium by the phenylanthranil method, 5 ml of the original phosphotungstovanadic acid solution was placed in a conical flask of 50 ml capacity, and 10 ml of a mixture consisting of sulfuric acid

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* With the participation of Z. P Printsman and A. D. Berezina.

(d 1.84), phosphoric acid (d 1.7) and water, taken in equal volumes, was added. Two ml of concentrated HCl_3 was added and the mixture was evaporated until sulfuric acid vapors appeared; in this way decomposition of the heterotriacid proceeded. Tungsten was calculated quantitatively by difference.

Results of the analysis are presented in Table 2.

TABLE 2

Composition of the Phosphotungstovanadic Acid Obtained

Sample No.	Composition of the complex						H_2O (%)	Ratios $P : W : V : H_2O$
	P		W		V			
	mg	mg-at	mg	mg-at	mg	mg-at		
1	0.81	0.026	46.0	0.25	2.65	0.052	18.2	1 : 9.5 : 2 : 31
2	0.74	0.024	44.2	0.24	2.19	0.043	23.2	1 : 10 : 1.8 : 38
3	0.72	0.023	41.4	0.225	2.40	0.047	15.8	1 : 9.8 : 2 : 27

Based on the data obtained, the compound might be expressed by the formula: $H_7[P(W_2O_7)_5V_2O_6] \cdot nH_2O$, where the number of water molecules, (n), may be from 27 to 38.

SUMMARY

1. The optimal conditions for synthesis of phosphomolybdenovanadic and phosphotungstovanadic acids were determined, and methods of analysis were developed.

2. On the basis of the compositions determined for the heterotriacids, the compounds might be expressed by the formulas: $H_7[P(Mo_2O_7)_5V_2O_6]$ and $H_7[P(W_2O_7)_5V_2O_6]$.

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HETEROTRIACIDS

II. SILICOMOLYBDOVANADIC ACID

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Heterodiacids having a central atom of silicon have been well-known for a relatively long time. Reactions forming the silicomolybdo complex, for example, have attained widespread use in the colorimetric determination of silicon. Silicomolybdic and silicotungstic acids have been used successfully for separating and determining rubidium and cesium, for detecting potassium, for precipitating the alkaloids, and for a number of other analytical purposes.

The number of works devoted to the heterotriacids containing silicon is extremely limited. Moreover, by analogy with phosphomolybdovanadic acid it is essential to assume that silicomolybdovanadic acid is considerably more reactive than silicomolybdic acid.

The purpose of the present work was the determination of the optimal conditions of synthesis of silicomolybdovanadic acid by the ester method, establishment of the composition of the synthesized acid, and investigation of some of its properties.

SYNTHESIS

For determining the optimal conditions of synthesis, it was necessary first of all, to account for the effect of the starting materials, their quantitative proportions, the acidity of the medium during formation of the complex anion and the ester, and also, the effect of the order of addition of the reagents used, and the effect of the temperature conditions on the yield of synthesized product.

The main difficultly in the synthesis of the present heterotriacid appeared to be the formation, in acid medium, of precipitates of silicic acid, molybdic anhydride and vanadic anhydride. If, for the synthesis of phosphomolybdovanadic acid, molybdic and vanadic anhydrides are used as starting materials, provided that a considerable excess of phosphoric acid is used, the synthesis of silicomolybdovanadic acid from the anhydrides gives no positive results. The synthesis proceeds very successfully when crystalline sodium silicate, molybdic acid and sodium metavanadate are used as starting materials. The substitution of molybdic acid for sodium molybdate is possible provided that a suitable acidity is established. The substitution of the ortho-vanadate for the meta-vanadate is not desirable.

During the process of synthesis, special attention should be paid to maintenance of a strictly determined acidity, which in the initial stage should be as low as possible. When using molybdic acid, a supplementary introduction of another acid appears to be detrimental. The optimal acidity for production of the ester of silicomolybdovanadic acid corresponds to that of 6 N sulfuric acid.

It is necessary to use an excess of vanadate in order to obtain the most complete reaction. However, an excess that is more than 2 times the stoichiometric quantity leads to considerable contamination of the ester precipitate by vanadic anhydride, which complicates the operation considerably.

Calculations were made, proceeding from the proposed formula, $H_8[Si(Mo_2O_7)_5V_2O_6] \cdot \underline{x}H_2O$, of the synthesized compound.

For best reaction, the sodium silicate and the sodium meta-vanadate should be first dissolved in suitable quantities of water. The synthesis proceeds to completion by boiling for a period of 2 hours. As a consequence of the considerable instability of the ester and the great oxidation capacity of the synthesized compound, a very careful and relatively rapid and complete removal of ether is required. Crystallization was carried out from aqueous solution at room temperature, protecting the solution from the entrance of dust, ammonia vapors, hydrogen sulfide vapors, etc.

Proceeding from the above-mentioned conditions, apparent as a result of the preliminary investigation, the procedure cited below is adopted for the synthesis of silicomolybdovanadic acid.

Eleven grams of $NaVO_3$, first dissolved by heating in 100 ml of water, and 31 g of $H_2MoO_4 \cdot H_2O$ were added to 5 g of $Na_2SiO_3 \cdot 9H_2O$ dissolved in 125 ml of water. The mixture was placed in a flask fitted with a ground-in reflux condenser and subjected to a 2-hour boiling. Thus, after 20 minutes the molybdic acid was completely dissolved, and the solution acquired an intense red color. After cooling, the solution was transferred to a separatory funnel into which 100 ml of ether had been previously introduced. After shaking, a small portion of H_2SO_4 (1:1) was added, with careful stirring. In case of the formation of a turbid mixture, the stirring was continued until clarification of the solution was complete, and only after this were new portions of sulfuric acid added. The first drops of the heavy, oily liquid – the ester of the heterotriacid – formed on introduction of 70 ml of H_2SO_4, which corresponds to 4 N sulfuric acid. Formation of the ester ceased completely on addition of 115 ml of H_2SO_4, which corresponds to 6 N acid. After a period of several hours of settling, the ether and water layers acquired a yellow color, and the lower ester layer – a red color. The washing of the ester was carried out in another separatory funnel using 6 N H_2SO_4, saturated with ether. After allowing it to settle well, the lower layer was transferred to a crystallizer, small portions of 4-5 ml of water were added, and the ether was completely removed by cautious warming over a heated water bath. A high temperature often leads to decomposition of the heterotriacid – to formation of products of a black color. After careful removal of the ether, the aqueous solution remaining was crystallized at room temperature. Crystallization was accomplished in 3-4 hours. The crystals were filtered from the mother solution through a filter having a porous quartz plate, and dried on a watch glass. The silicomolybdovanadic acid, dried at room temperature, consists of the red-colored crystal hydrate, which it is necessary to store in a dark bottle with good ground-glass stopper.

ANALYSIS

Silicon. For determination of the silicon content, a weighed portion (about 1 g) of the heterotriacid was placed in a fired (at 450°) and weighed platinum crucible and carefully heated in an air bath in order to remove the larger part of the water of crystallization. Then, at a higher temperature the water of constitution was removed, after which the crucible with residue was covered and fired at 450°. The heterotriacid, reduced by calcination (the residue turned green) was oxidized carefully by several drops of concentrated HNO_3. After removal of the latter, a calcination to constant weight was carried out. The oxides obtained were treated with 2-3 drops of H_2SO_4 (1:2) and 5 ml of hydrofluoric acid before carefully heating until sulfuric acid vapors appeared, and then were calcined to a constant weight at 450°. The treatment of the liquefied acid was repeated twice. From the decrease in weight, the silicon dioxide content was calculated.

Determination of vanadium and molybdenum. In a single experiment this determination was carried out on the residue after treatment of the molten acid, by dissolving it in concentrated HCl and diluting it in a volumetric flask. Vanadium was determined in the presence of molybdenum by titration with permanganate, after evaporating an aliquot portion with a mixture of sulfuric and phosphoric acids and reducing the vanadium with hydrochloric acid. In another experiment, after separating vanadium by means of caustic soda in the presence of a mixture of ferrous and ferric sulfates, molybdenum was determined as lead molybdate. In other experiments vanadium was determined by titration of the pentavalent vanadium by ferrous sulfate, in the presence of sulfuric and phosphoric acids, by the phenylanthranil method. Determination of vanadium by a different method gave results that agreed completely. Determination of molybdenum by the plumbate method required more time for completion and was not sufficiently accurate.

As shown by the investigations made, the determination of molybdenum and vanadium in silicomolybdovanadic acid may be carried out rapidly and entirely satisfactorily from a separate weighed portion, analogous to that described for the analysis of phosphomolybdovanadic acid.

A weighed portion of 1.5-2 g of the sample to be analyzed was dissolved in a volumetric flask of 100 ml capacity. A tenth of the solution obtained was treated by boiling with 10 ml of H_2SO_4 (1:1), in order to decompose the heterotriacid. Thus, the silicon in the residue did not precipitate, but remained in the colloidal condition. The solution was washed with 10 ml of water into a previously prepared apparatus for reduction, and molybdenum and vanadium were reduced by zinc amalgam in an atmosphere of carbon dioxide. Oxidation by ferric ammonium alum, titration with potassium permanganate, and further titration with a solution of Mohr's salt in the presence of phenylanthranilic acid was carried out completely in accordance with the procedure given earlier.*

Results of the analysis are given in the table, in which, for the sake of brevity, only those weighed portions of the samples analyzed are considered which were taken for determination of silicon, and for which also calculations of the molybdenum and vanadium contents were made on other weighed portions.

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* J. Gen. Chem., 24, 966 (1954). [See Consultants Bureau Translation, page 967].

TABLE

Result of the Analysis of Silicomolybdovanadic Acid

Expt. No.	Weighed portion (g)	Sum of oxides (g)	SiO_2		MoO_3		V_2O_5		Ratio
			(g)	(mole)	(g)	(mole)	(g)	(mole)	$SiO_2 : MoO_3 : V_2O_5$
1	0.998	0.760	0.027	0.00044	0.651	0.0045	0.084	0.00045	1 : 10.2 : 1.04
2	0.938	0.715	0.026	0.00043	0.612	0.00425	0.079	0.00043	1 : 9.9 : 1.0
3	1.029	0.786	0.028	0.00046	0.673	0.0047	0.086	0.00047	1 : 10.2 : 1.02

The content of water of crystallization was determined by drying and by the hydride method. For a given sample it amounted to 18-19%, at the same time as the loss on calcination (i.e., the total content of water) was equal to 23.6-23.8%.

On the basis of the analytical data obtained, the synthesized compound may be expressed by the formula, $H_8[Si(Mo_2O_7)_5V_2O_6] \cdot 24H_2O$.

In contrast to silicomolybdic acid, silicomolybdovanadic acid did not form precipitates with silver nitrate and rubidium chloride. The oxidation capacity of silicomolybdovanadic acid is considerably higher than that of silicom~~oly~~bdic: in acid medium it is reduced to a colored compound by the divalent iron cation in the presence of sulfurous acid; reduction also proceeds in the cold on treatment with the trivalent antimony cation. The latter property of silicomolybdovanadic acid also differs favorably from that of phosphomolybdic acid, solutions of which are reduced by trivalent antimony only on heating. It is fundamental to assume that silicomolybdovanadic acid is shown to be a new reagent for the quantitative colorimetric determination of antimony.

SUMMARY

1. The optimal conditions of synthesis of silicomolybdovanadic acid by the ester method were determined.

2. The composition of the indicated heterotriacid was determined, and on that basis the compound obtained may be expressed by the formula:

$$H_8[Si(Mo_2O_7)_5V_2O_6] \cdot \underline{n}H_2O.$$

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COMPLEX CUPRIC SALTS OF α-HYDROXYACIDS

I. TRITARTRATOTETRACUPROATES OF COMPLEX CATIONS OF COBALT AND CHROMIUM

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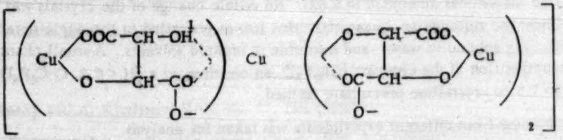
It is well-known that an alkali does not precipitate copper ion in the presence of tartrate ions. Moreover, some investigators [1] consider the solutions obtained as colloidal; however, the majority [2, 3] assume that complex compounds form. Until now the attention of most investigators has been devoted to the complex compounds forming in alkaline solutions. Thus, quite a few works have been devoted to the complexes found in Fehling's solution [2]. The complex salts of polybasic α-hydroxyacids, occurring in neutral media, have been studied less. Recently, a number of authors have developed volumetric methods for determining the ions of aluminum [4], iron [5], beryllium [6], zinc [7], copper [8], etc., which are based on the formation of tartrate and citrate complexes, which are stable in neutral media. In order to ground these methods completely it is necessary to know the nature of the complex compounds formed by the α-hydroxyacid with the metal, present in neutral medium.

A rather large number of works has been devoted to studies of the complex combination of tartaric acid and copper occurring in neutral solutions. From neutral solutions, containing copper ion and tartrate ion, crystalline products have been separated, the compositions of which different authors write as: Na_2CuT, $Na_3Cu_4T_3$ [9], Na_2CuT_2, CuCuT.* On the basis of physico-chemical investigations, it was assumed that the following exist in these solutions: CuT^-, $Cu_2T_2^{--}$ [1, 3]. The existence of many of these compounds is doubtful. In all the works referred to, a readily soluble salt of cupritartaric acid with an alkali metal was isolated.

In our work we set the goal of obtaining a crystalline salt, difficultly soluble in water, and having a bulky cation. We proceeded from the assumption that, with favorable charge and volume ratios of complex cupritartrate anion and cation, a difficultly soluble salt might form.

Actually, by preparing a strictly neutral solution containing the complex cupritartaric acid anion, we obtained very difficultly soluble crystalline products of the composition, Cat. $Cu_4T_3 \cdot nH_2O$, by the addition of complex trivalent cations of cobalt and chromium. The salts obtained, as well as the salts with simple cations (sodium, barium), contain a large number of water molecules. The water is lost with difficulty, and not completely, neither by heating to 100-105° nor in vacuo over phosphorus pentoxide.

The unusual stability of a neutral solution of a salt of cupritartaric acid toward heating compels one to write the anion $[Cu_4T_3]^{3-}$ as a symmetrical structure and consider its polynuclear compounds, probably, as having the following structure:



The stability of the anion depended on the presence of a six-membered ring. It should be pointed out that the assumed formula actually appears to be completely symmetrical, since the hydrogen, designated by the figure 1, is not restricted to one oxygen. It is possible that this accounts for the unusual susceptibility of this complex anion toward acids and alkalis. The three "peripheral" copper atoms in the complex anion undoubtedly coordinate water molecules, but since there is no possibility of judging their number, it seems to us the salt is represented better as containing the $[Cu_4C_{12}H_7O_{18}]^{3-}$ anion. Furthermore, we call the salt including this anion, tritartratotetracuproate.

Messon [9] and other authors represent this anion with one molecule of water, $[Cu_4C_{12}H_9O_{19}]^{3-}$.

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* T is the tartaric acid radical.

EXPERIMENTAL

Preparation of the solution containing the complex anion of cupritartaric acid. Copper tartrate dissolves in a dilute solution of alkali, for which, in order to produce a strictly neutral solution, 1.25 moles of potassium hydroxide is required for 1 mole of copper tartrate [10]. Formation of the complex anion proceeds according to the equation:

$$4CuC_4H_4O_6 + 5HOH^- = [Cu_4C_{12}H_7O_{18}]^{3-} + C_4H_4O_6^{2-} + 5H_2O.$$

As seen from a potentiometric titration curve [10], the cupritartaric acid forming in the solution seemed to be a strong acid. The presence of tartrate ions stabilized the complex cupritartaric acid anion. The fact that copper enters into the composition of the complex anion was demonstrated by electrolysis [9] and by measuring the E. M. F. of the circuit. The anion in solution was very stable toward heat. Hydrogen ions decomposed the cupritartaric acid anion.

We found that if we mixed a dilute solution of an alkali metal tartrate, taken in excess, with a solution of a copper salt of a strong acid, the liquid acquired a distinctly acid reaction. By neutralization with alkali, the liquid acquired a blue-green color and no precipitate of copper hydroxide separated. It is possible to represent the formation of the copper complex, tritartratotetracuproate ion, by the following equation:

$$3C_4H_4O_6^{2-} + 4Cu^{2+} = [Cu_4C_{12}H_7O_{18}]^{3-} + 5H^+.$$

For stabilization of the tritartratotetracuproate ion forming, an excess of tartrate ion was undoubtedly necessary.

Furthermore, for preparation of the initial solution, containing the tritartratotetracuproate ion, we followed the procedure indicated: 5.00 g of potassium tartrate ($K_2C_4H_4O_6 \cdot \frac{1}{2}H_2O$) and approximately 1.3 g of potassium hydroxide were dissolved in 50 ml of water. To the solution, heated to 50-60°, a solution of 3.41 g of cupric chloride, $CuC_{12} \cdot 2H_2O$, in 25 ml of water was added dropwise. The cupric hydroxide that separated dissolved on stirring. To the filtered solution was added a solution of potassium hydroxide diluted to a pH of 6.6-7.

It was assumed that all the copper in the solution was in the form of the tritartratotetracuproate ion. No tartrate ion, necessary for stabilization of the solution (1.2 tartrate ions to 4 copper atoms), was found to be combined with this complex anion in solution.

1. Hexammonocobalti-tritartratotetracuproate, $[Co(NH_3)_6][Cu_4C_{12}H_7O_{18}] \cdot 15H_2O$. This salt, as also the following, was obtained by mixing a solution of tritartratotetracuproate with a small excess of the complex cobalt salt (to 4 moles of copper, somewhat more than 1 mole of cobalt was taken). To the solution, heated to 60°, 1.5 g of hexammonocobaltichloride in 50 ml of water was added dropwise with constant stirring and heating to 50-60° the tritartratotetracuproate solution prepared according to the indicated method, starting from 3.41 g of copper chloride. Green crystals separated on slow cooling. The crystals were washed several times by decantation with water, transferred to a glass filter and washed with water until chloride disappeared; then they were dried in air. The yield was 4.35 g (the theoretical amounted to 5.62). No visible change of the crystals was observed during washing with water. Under the microscope, hexagonal thick leaves prevailed in the agglomeration of crystals. The substance was difficultly soluble in water and insoluble in organic solvents. A small change of the pH of the medium led to the decomposition of the complex $[Cu_4T_3]^{3-}$ anion; thus, at a pH < 6.2, $CuC_4H_4O_6 \cdot 3H_2O$ crystals separated, but at a pH > 7.2 no crystalline precipitate formed.

The air-dried substance from different experiments was taken for analysis.

0.4018 g sub.: 0.1765 g CuSCN; 0.1765 g $[CoPy_4(NCS)_2]$. 0.3803 g sub.: 0.1672 g CuSCN; 0.1670 g $[CoPy_4(NCS)_2]$. 0.3324 g sub.: 0.1460 g CuSCN. 0.4134 g sub.: 0.1938 g CO_2; 0.1809 g H_2O. 0.4712 g sub.: 0.2215 g CO_2; 0.2073 g H_2O. Found %: Cu 22.98, 22.98, 22.96; Co 5.27, 5.27; C 12.79, 12.83; H 4.90, 4.92. $[Co(NH_3)_6][Cu_4C_{12}H_7O_{18}] \cdot 15H_2O$. Calculated %: Cu 22.59; Co 5.24; C 12.81; H 4.93.

After heating in a drying chamber at 100-105° for a period of 45 hours, the substance lost in weight:

0.3802 g sub.: loss 0.0814 g. 0.4477 g sub.: loss 0.0938 g. Found %: H_2O 21.40, 20.95.

During a period of 14 days, over P_2O_5, at room temperature, the substance lost in weight:

0.4804 g sub.: loss 0.1048 g. 0.4531 g sub.: loss 0.0993 g. Found %: H_2O 21.81, 21.92. Calculated %: H_2O 22.42 for $[Co(NH_3)_6][Cu_4C_{12}H_9O_{19}] \cdot 14H_2O$, 24.02 for $[Co(NH_3)_6][Cu_4C_{12}H_7O_{18}] \cdot 15H_2O$.

The losses in weight agree better with the first formula, including one molecule of water in the composition of the complex $[Cu_4C_{12}H_9O_{19}]^{3-}$ anion.

2. Triethylenediaminecobalti-tritartratotetracuproate, $[Coen_3][Cu_4C_{12}H_7O_{18}] \cdot 11H_2O$. It was obtained, like the previous salt, starting from $[Coen_3]Cl_3 \cdot 3H_2O$. It consisted of yellowish-green hexagonal plates, difficultly soluble in water.

0.4754 g sub.: 0.2042 g CuSCN; 0.2038 g $[CoPy_4(NCS)_2]$. 0.3580 g sub.: 0.2492 g CO_2; 0.1543 g H_2O. Found %: Cu 22.45; Co 5.14; C 19.00; H 4.82. $[Co(C_2H_8N_2)_3][Cu_4C_{12}H_7O_{18}] \cdot 11H_2O$. Calculated %: Cu 22.45; Co 5.21; C 19.05; H 4.72.

3. Aquapentammonocobalti-tritartratotetracuproate, $[Co(NH_3)_5H_2O][Cu_4C_{12}H_7O_{18}] \cdot 13H_2O$. For preparation of this salt it was possible to start from the crystalline aquapentammono-salt. It was simpler, however, to follow this procedure: 2 g of chloropentammonocobaltichloride, $[Co(NH_3)_5Cl]Cl_2$, was dissolved, with slight heating, in 50 ml of 2.4% ammonia. Hydrochloric acid was added to the filtered solution until the pH = 6.8-7. The neutral solution was mixed with a solution of tritartratotetracuproate. The mixture acquired an intense reddish-violet color. After 12 hours, the large blue crystals precipitated were transferred to a filter, washed with water until chloride ion was removed, and dried in the air. The yield was 4.15 g. Under the microscope the crystals were hexagonal, elongated plates. The substance was difficultly soluble in water. It decomposed on heating to 130-140°.

0.3865 g sub.: 0.1720 g CuSCN; 0.1736 g $[CoPy_4(NCS)_2]$. 0.4045 g sub.: 0.1807 g CuSCN; 0.1814 g $[CoPy_4(NCS)_2]$. 0.3873 g sub.: 0.1883 g CO_2; 0.1556 g H_2O. 0.4960 g sub.: 0.2398 g CO_2; 0.2013 g H_2O. Found %: Cu 23.26, 23.24; Co 5.39, 5.38; C 13.27, 13.19; H 4.50, 4.54. $[Co(NH_3)_5H_2O][Cu_4C_{12}H_7O_{18}] \cdot 13H_2O$. Calculated %: Cu 23.30; Co 5.40; C 13.22; H 4.62.

During warming in a drying chamber at 100-105° for a period of 54 hours, the substance lost in weight:

0.5007 g sub.: loss 0.0902 g. 0.3221 g sub.: loss 0.0590 g. Found %: H_2O 18.01, 18.32. Calculated %: H_2O 19.84 for $[Co(NH_3)_5H_2O][Cu_4C_{12}H_9O_{19}] \cdot 12H_2O$, 21.49 for $[Co(NH_3)_5H_2O][Cu_4C_{12}H_7O_{18}] \cdot 13H_2O$.

4. Hexacarbamidechromi-tritartratotetracuproate, $[Cr(NH_2CONH_2)_6][Cu_4C_{12}H_7O_{18}] \cdot 18H_2O$. In order to obtain this salt, 2 g of hexacarbamidechrominitrate, $[Cr(NH_2CONH_2)_6](NO_3)_3$, was dissolved in 50 ml of water, heated to 60-70°, and tritartratotetracuproate, prepared by starting from 3.41 g of $CuCl_2 \cdot 2H_2O$, was added to it dropwise. Coarse, light-bluish plates in the form of rhombs separated from the solution on cooling.

0.2991 g sub.: 0.1026 g CuSCN. 0.1882 g sub.: 0.0522 g CuO + Cr_2O_3. 0.2845 g sub.: 0.0973 g CuSCN. 0.2371 g sub.: 0.0655 g CuO + Cr_2O_3. 0.3771 g sub.: 0.2094 g CO_2; 0.1633 g H_2O. 0.3090 g sub.: 0.1731 g CO_2; 0.1349 g H_2O. 0.3838 g sub.: 0.2195 g CO_2; 0.1630 g H_2O. Found %: Cu 17.93, 17.87; Cr 3.64, 3.57; C 15.16, 15.25, 15.61; H 4.84, 4.88, 4.75. $[Cr(CH_4ON_2)_6][Cu_4C_{12}H_7O_{18}] \cdot 18H_2O$. Calculated %: Cu 17.77; Cr 3.64; C 15.12; H 4.73.

SUMMARY

1. Crystalline salts of the composition Cat. Cu_4T_3, were obtained from neutral solutions containing divalent copper and an excess of tartrate ion, added to bulky trivalent complex cations of cobalt and chromium.

2. It was demonstrated that the complex anion $[Cu_4T_3]^{3-}$ is present in neutral media.

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BISMUTH AMINES, THEIR STRUCTURE AND FORMATION IN AQUEOUS SOLUTIONS

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As is well-known, the ammoniates and amines of a series of metals (copper, cadmium, zinc, nickel, cobalt, etc.), are easily dissolved in water and are formed by the addition of an excess of ammonia, or of some suitable amine, to an aqueous solution of a salt of the indicated metal. Formation of the amines of bismuth in aqueous solutions is considerably hampered, since the majority of bismuth salts easily undergo hydrolysis by the action of water; therefore, the ammoniates and amines of bismuth are obtained either by the action of gaseous [1] or liquid [2] ammonia on a bismuth salt, or by the action of a solution of an amine [3] in an anhydrous organic solvent (acetone, ether, alcohol) on such a bismuth salt solution. The indicated method of obtaining the bismuth amines is, in many cases, not practicable because of the insolubility of the majority of bismuth salts in organic solvents.

However, the possibility of forming bismuth amines in aqueous solutions was shown both by investigations that we carried out [4, 5], with citrate and tartrate, and by the investigations of Izmailsky and coworkers [6] with bismuth tartrate. We attempted to obtain the amines from water-soluble complex salts, based on the fact that it is possible to consider their aqueous solutions as solutions of simple BiX_3 salts in neutral solvents in accordance with the equation:

$$Me_{n-3}[BiX_n] \rightleftharpoons BiX_3 + (n-3)\,MeX \qquad (1)$$

(n is the coordination number of the bismuth atom).

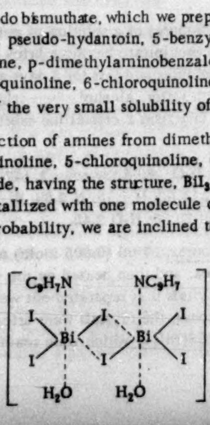
Preliminary investigations showed that, actually, solutions of $BiCl_3$ in concentrated NH_4Cl solution, $Bi_2(SO_4)_3$ in $(NH_4)_2SO_4$ solution, and others, form crystalline amine precipitates with a series of amines. Precipitation of the amines disrupts the equilibrium of the secondary dissociation, represented by equation (1), so that the complex salt can be completely converted to the corresponding amine:

$$a\,Me_{n-3}[BiX_n] + b\,RNH_2 \longrightarrow a\,BiX_3 \cdot b\,RNH_2 + (n-3)\,MeX. \qquad (2)$$

For the purpose of preparation we discontinued the use of potassium iodobismuthate prepared by the action of a large excess of potassium iodide on neutral bismuth nitrate, since the amines of bismuth iodide are more stable toward the hydrolytic action of water. Such a reagent was prepared almost neutral, in contrast to the generally well-known Dragendorff [7] reagent, containing, as a result of the addition of nitric acid, free iodobismuthic acid, $HBiI_4$. On reaction of the Dragendorff reagent on organic bases, crystalline iodobismuthates, but not amines, form.

The neutral solution of potassium iodobismuthate, which we prepared forms a crystalline precipitate on grinding in the cold or on heating with urotropine, pseudo-hydantoin, 5-benzylidene-pseudo-thiohydantoin, β-picoline, thiourea, dimethylaniline, p-nitroso-dimethylaniline, p-dimethylaminobenzaldehyde, p-aminosalacylic acid, tetramethyldiaminobenzophenone, quinoline, 5-chloroquinoline, 6-chloroquinoline, 6-aminoquinoline, etc.. Some of the amines of bismuth iodide do not form because of the very small solubility of the amines in water or as a result of hydrolysis (for example, aniline).

In this paper we describe the production of amines from dimethylaniline, diethylaniline, p-nitrosodimethylaniline, p-dimethyl. aminobenzaldehyde, quinoline, 5-chloroquinoline, 6-aminoquinoline, cordyl amine and thiourea. Of these, the quinolinate of bismuth iodide, having the structure, $BiI_3 \cdot C_9H_7N$, is described in the literature [8]. We produced a similar compound which crystallized with one molecule of water. Since the existence of the coordination number V for the bismuth atom is of small probability, we are inclined to adopt the following dimeric structure having a coordination number of VI:

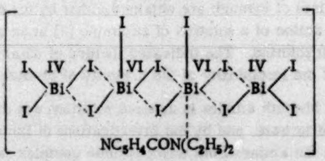


For the same reason Dubsky and coworkers [9], and also Gutbier and Müller [10], used the dimeric structure for chloro- and bromo-bismuthates.

The dimeric structure should also be adopted for compounds of thiourea with bismuth iodide, $4CS(NH_2)_2 \cdot 2BiI_3$, although in the present case a secondary bond with the sulfur atom might also develop. In the literature bismuth iodide compounds including one [11] and three [12] molecules of thiourea are described.

The coordination number VI is involved also in the molecule of the compound which is formed by dimethylaminobenzaldehyde, $3(CH_3)_2NC_6H_4CHO \cdot BiI_3$. The trinuclear structure and the coordination number VI are present in the molecule of bismuth iodide dimethylanilinate, $2(CH_3)_2NC_6H_5 \cdot 3BiI_3$.

The quadrinuclear structure is characteristic of the compounds formed by diethylaniline, $3(C_2H_5)_2NC_6H_5)_2 \cdot 4BiI_3$; cordyl amine, $C_5H_4NCON(C_2H_5)_2 \cdot 4BiI_3$; 6-aminoquinoline, $3NH_2C_9H_6N \cdot 4BiI_3$; 5-chloroquinoline, $6ClC_9H_6N \cdot 4BiI_3$ and p-nitrosodimethylaniline, $6NOC_6H_4N(CH_3)_2 \cdot 4BiI_3$. In the two latter cases we adopt the double formulas for the same reason, which is also true in the case of the quinolinate. In all the compounds indicated, the coordination number of the bismuth atom is equal to VI. Aminoquinoline and cordyl amine occupy two coordination positions on introduction of two nitrogen atoms. The combination of cordyl amine with bismuth iodide, apparently, has the structure



in which the coordination number of the bismuth atoms connected with nitrogen is equal to VI.

It should be pointed out that we demonstrated the polynuclear structure for some complex compounds of bismuth (among them also ammoniates) by heating [13], and also by carrying out a multi-stage hydrolysis [14]. We did not follow the hydrolysis of the bismuth iodide amines, because the compounds that we obtained seemed to be either very stable or too rapidly hydrolyzed in water. Thus, we obtained the crystalline amine for m-toluidine, but on washing the potassium nitrate from it with water, we observed its complete conversion to BiOI.

During investigation of the physical properties of the amines of bismuth iodide, we observed the very rare phenomenon of the solubility of the complex bismuth compound in organic solvents. Thus, the addition products of dimethylaminobenzaldehyde and thiourea to BiI_3 dissolved rather readily in ether, acetone and alcohol.

EXPERIMENTAL

Potassium iodobismuthate solution. 99.6 g (0.6 mole) of potassium iodide was triturated with 48.4 g (0.1 mole) of crystalline bismuth nitrate in a porcelain mortar. To the pasty mass obtained, 150 ml of water was added in several portions. The reddish-orange solution was filtered and collected in a place which was protected from the light. The composition of the solution was potassium iodo-bismuthate, potassium nitrate and an excess of potassium iodide. In 1 ml of solution after diluting and colorimetrically comparing with a standard solution (0.1 g Bi per 1 ml) we found 295 mg of BiI_3.

Bismuth iodide quinolinate. 10 ml (0.005 mole) of a solution of potassium iodo-bismuthate was shaken with 2.58 g (0.02 mole) of quinoline, after which a precipitate having a brick color separated several minutes later. The mixture was heated on the water bath for 10 minutes and left for 2 days at room temperature. The precipitate was then filtered into a Büchner funnel, washed with water, alcohol ether; dried in the air. The yield was 3.1 g. The quinolinate of bismuth iodide, $2C_9H_7N \cdot 2BiI_3 \cdot 2H_2O$ was a crystalline substance, brick-red in color, and insoluble in water, alcohol and ether.

281.7 mg sub.: 151.0 mg CO_2: 28.9 mg H_2O. 60.8 mg sub.: 1.147 ml N_2 (23°, 731 mm). 311.7 mg sub.: 8.4 mg H_2O; 98.7 mg Bi_2O_3. Found %: C 14.63; H 1.15; N 2.09; Bi 28.40; H_2O 2.69. $2BiI_3 \cdot 2C_9H_7N \cdot 2H_2O$. Calculated %: C 14.67; H 1.23; N 1.90; Bi 28.36; H_2O 2.45.

Compound of bismuth iodide with thiourea. 10 ml (0.005 mole) of potassium iodobismuthate was triturated in a 25 ml flask with 1.56 g (0.02 mole) of urea, and then heated on the water bath for a period of 10 minutes. The clear solution obtained was cooled, and the crystals that separated out were filtered into a Büchner funnel. After washing with water and a small amount of alcohol, the crystals were dried in the air. We obtained 1.8 g of large dark orange crystals of the compound $2BiI_3 \cdot 4CS(NH_2)_2$, which were readily soluble in ether, alcohol, acetone, and slightly soluble in benzene.

236.5 mg sub.: 30.4 mg CO_2; 23.3 mg H_2O. 193.0 mg sub: 60.9 mg Bi_2O_3; 7.8 ml 0.1 N $AgNO_3$. Found %: C 3.51; H 1.10; Bi 28.31; I 51.29. $2BiI_3 \cdot 4CS(NH_2)_2$. Calculated %: C 3.24; H 1.09; Bi 28.17; I 51.32.

The p-Nitrosodimethylanilinate of bismuth iodide. 10 ml (0.005 mole) of potassium iodobismuthate solution was triturated in a flask with 3.0 g (0.02 mole) of p-nitrosodimethylaniline, whereby crystals of amine were observed to form in the cold. The mixture was heated on the water bath for 20 minutes. After cooling, the precipitate was filtered off, washed with water, alcohol and ether, and dried in the air. We obtained 3.4 g of the brick-red crystalline substance, $4BiI_3 \cdot 6NOC_6H_4N(CH_3)_2$, which was not soluble in water, alcohol, or ether.

259.8 mg sub.: 167.5 mg CO_2; 44.2 mg H_2O. 155.8 mg sub.: 6.89 ml N_2 (25.5°, 733). 199.1 mg sub.: 57.2 mg Bi_2O_3; 7.3 ml 0.1 N $AgNO_3$. Found %: C 17.59; H 1.90; N 4.88; Bi 25.77; I 46.53. $4BiI_3 \cdot 6NOC_6H_4N(CH_3)_2$. Calculated %: C 17.68; H 1.86; N 5.16; Bi 25.64; I 46.72.

The 6-aminoquinolinate of bismuth iodide. 10 ml (0.005 mole) of potassium iodobismuthate solution and 2.88 g (0.02 mole) of 6-aminoquinoline were reacted as in the case of p-nitrosodimethylaniline. We obtained 2.5 g of the yellow-cinnamon colored substance $4BiI_3 \cdot 3NH_2C_9H_6N$, which was insoluble in water, alcohol and ether.

167.1 mg sub.: 73.1 mg CO_2; 17.8 mg H_2O. 115.3 mg sub.: 38.4 mg Bi_2O_3; 4.95 ml 0.1 N $AgNO_3$. Found %: C 11.94; H 1.19; Bi 29.87; I 54.49. $4BiI_3 \cdot 3NH_2C_9H_6N$. Calculated %: C 11.62; H 0.87; Bi 29.95; I 54.56.

The compound of cordyl amine with bismuth iodide. 10 ml (0.005 mole) of potassium iodobismuthate solution and 6 ml of a solution containing 2.44 g (0.02 mole) of cordyl amine, were poured together, and an amine precipitate deposited. The mixture was heated for 20 minutes on a water bath, and after cooling, the precipitate was filtered off, and washed with water and a large amount of alcohol. The preparation was dried in the air. We obtained 1.8 g of the substance $4BiI_3 \cdot C_5H_4NCON(C_2H_5)_2$, having a carmine red color, and insoluble in water, alcohol and ether.

485.1 mg sub.: 86.5 mg CO_2; 26.2 mg H_2O. 205.1 mg sub.: 74.8 mg Bi_2O_3; 9.7 ml 0.1 N $AgNO_3$. Found %: C 4.87; H 0.60; Bi 32.71; I 60.02. $4BiI_3 \cdot C_5H_4NCON(C_2H_5)_2$. Calculated %: C 4.73; H 0.56; Bi 32.95; I 60.03.

The compound of p-dimethylaminobenzaldehyde with bismuth iodide. 3.3 ml (0.0016 mole) of potassium iodobismuthate solution was introduced into reaction with 1 g (0.0067 mole) of p-dimethylaminobenzaldehyde, as in the case with thiourea. We obtained 1.6 g of brick-red crystals having the composition, $BiI_3 \cdot 3(CH_3)_2NC_6H_4CHO$. The preparation was soluble in alcohol, ether and acetone, and slightly soluble in benzene.

214.1 mg sub.: 243.2 mg CO_2; 59.9 mg H_2O. 92.8 mg sub.: 3.588 ml N_2 (20°, 753 mm). 101.0 mg sub.: 22.5 mg Bi_2O_3. Found %: C 31.00; H 3.13; N 4.34; Bi 19.98. $BiI_3 \cdot 3(CH_3)_2NC_6H_4CHO$. Calculated %: C 31.26; H 3.21; N 4.05; Bi 20.15.

The dimethylanilinate of bismuth iodide. 5 ml (0.0025 mole) of potassium iodobismuthate solution was triturated with 1.21 g (0.01 mole) of dimethylaniline in a 25 ml flask. Characteristic amine crystals were formed in the cold. The mixture was boiled for 2 minutes, and then cooled. The crystals were filtered off, washed with water, alcohol and ether, and dried in the air. We obtained 1.7 g of the substance $3BiI_3 \cdot 2(CH_3)_2NC_6H_5$, which had a brick-red color, and was insoluble in water, alcohol, and ether. On heating the preparation to 80° in a drying chamber, partial volatilization of the dimethylaniline was observed.

173.5 mg sub.: 58.1 mg CO_2; 19.2 mg H_2O. 52.3 mg sub.: 0.648 ml N_2 (19.5°, 733 mm). 118.9 mg sub.: 41.5 mg Bi_2O_3; 5.3 ml 0.1 N $AgNO_3$. Found %: C 9.14; H 1.24; N 1.40; Bi 31.31; I 56.58. $2(CH_3)_2NC_6H_5 \cdot 3BiI_3$. Calculated %: C 9.55; H 1.10; N 1.39; Bi 31.17; I 56.78.

The diethylanilinate of bismuth iodide. 5 ml (0.0025 mole) of potassium iodobismuthate solution was reacted with 1.49 g (0.01 mole) of diethylaniline, in a way similar to that of the preceding preparation. We obtained 1.2 g of the substance, $4BiI_3 \cdot 3(C_2H_5)_2NC_6H_5$, which had a brick-red color, and was insoluble in water, alcohol and ether. Also, like the preceding preparation, diethylaniline was volatilized from the substance on heating.

151.1 mg sub.: 68.9 mg CO_2; 21.4 mg H_2O. 21.8 mg sub.: 0.277 ml N_2 (21°, 730 mm). 156.3 mg sub.: 51.9 mg Bi_2O_3; 6.7 ml 0.1 N $AgNO_3$. Found %: C 12.44; H 1.58; N 1.41; Bi 29.79; I 54.40. $4BiI_3 \cdot 3(C_2H_5)_2NC_6H_5$. Calculated %: C 12.83; H 1.62; N 1.50; Bi 29.78; I 54.27.

The 5-chloroquinolinate of bismuth iodide. 2.5 ml (0.0012 mole) of potassium iodobismuthate solution was reacted with 0.8 g (0.005 mole) of 5-chloroquinoline in a way similar to that used for the two preceding preparations. We obtained 0.9 g of a dark orange product, $4BiI_3 \cdot 6ClC_9H_6N$, which was insoluble in water, alcohol and ether. On heating to 100° in a drying chamber, a partial volatilization of 5-chloroquinoline was observed.

143.6 mg sub.: 102.1 mg CO_2; 15.5 mg H_2O. 82.6 mg sub.: 1.715 ml N_2 (22°, 738 mm). 119.0 mg sub.: 33.4 mg Bi_2O_3. Found %: C 19.40; H 1.21; N 2.33; Bi 25.18. $4BiI_3 \cdot 6ClC_9H_6N$. Calculated %: C 19.41; H 1.09; N 2.52; Bi 25.02.

SUMMARY

1. The amines of bismuth iodide were obtained by reaction of amines with neutral aqueous solutions of potassium iodobismuthate.

2. The coordination number of the bismuth atom in its amine molecules is VI.

3. The majority of the bismuth iodide amines obtained have a polynuclear structure.

4. The addition compounds of bismuth iodide with p-dimethylaminobenzaldehyde and thiourea were characterized by their solubility in organic solvents.

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CATALYTIC SYNTHESIS OF KETONES

II. SYNTHESIS OF METHYL BUTYL KETONES AND METHYL ETHYL KETONE

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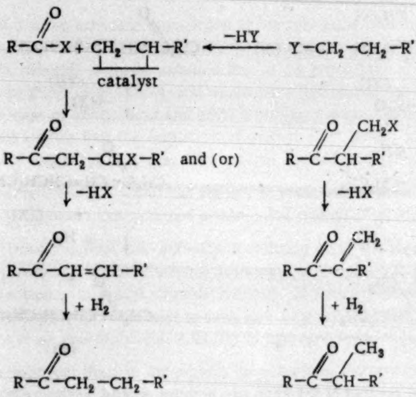
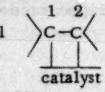
As shown earlier [1], upon the interaction of an acid with an alcohol over a catalyst, one should expect the formation of ketones of such structure that both radicals – the acidic and the alcoholic – are preserved. It was assumed that the alcohol molecule was initially dehydrated and simultaneously adsorbed by the catalyst, and that addition to the acid molecule proceeded later. The scheme of the reaction was presented in [2].

One may assume that in other analogous cases the formation of ketones from the corresponding acid derivatives and substituted hydrocarbons also proceeds according to the general scheme:



where X and Y may be: H, halides, OH, OR, OCOR, apparently NH_2, NR_2-groups, etc.; Y may occur as primary, secondary and tertiary carbon atoms.

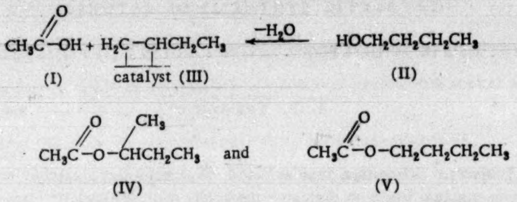
In the case of the halide derivatives, as will be shown below, the given reaction mechanism was essentially verified.

For the ketonization process, apparently, it is also necessary that the reacting molecules adsorbed by the catalyst be contacted at a minimum of two points. In the case of alcohol or alkyl halide molecule, the liberated bonds formed by dehydration or by the splitting off of hydrogen halide, add to the surface of the catalyst, and might be designated by the symbol  . To this adsorbed molecule may be added other reacting molecules, for example, acid, whereby addition may proceed in two directions, depending on the temperature (i.e., the energetic factor) and on steric factors. The breaking of the bond in the acid molecule may take place between the hydrogen and the oxygen, as a result of which an ester will form, or the rupture may occur between the OH and C groups – in this case a hydroxy ketone forms.

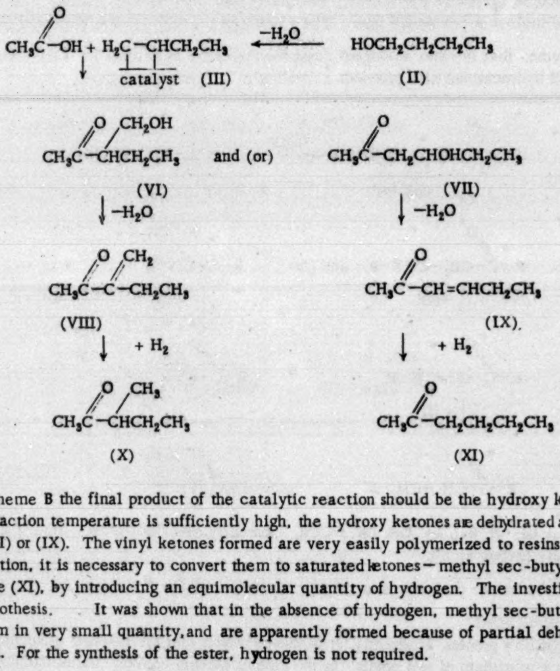
In the present work, to confirm this hypothesis, we carried out ketonization and esterification in mixtures of: 1) acetic acid and n-butyl alcohol in the presence of hydrogen over a chrome-manganese catalyst [3], applied to activated carbon; 2) acetyl chloride and ethyl bromide over manganese chloride, applied to asbestos wool, in the presence and absence of hydrogen.

It was assumed that in the case of acetic acid and n-butyl alcohol, at low temperature, an ester should form according to scheme A, and at high temperature, a ketone according to scheme B.

A.

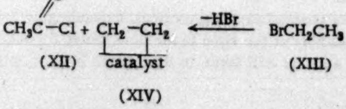


B.



According to scheme B the final product of the catalytic reaction should be the hydroxy ketones (VI) and (VII), but since the reaction temperature is sufficiently high, the hydroxy ketones are dehydrated and converted to the vinyl ketones (VIII) or (IX). The vinyl ketones formed are very easily polymerized to resins. In order to prevent their polymerization, it is necessary to convert them to saturated ketones – methyl sec-butyl ketone (X) and methyl n-butyl ketone (XI), by introducing an equimolecular quantity of hydrogen. The investigation made confirmed the given hypothesis. It was shown that in the absence of hydrogen, methyl sec-butyl ketone and methyl n-butyl ketone form in very small quantity, and are apparently formed because of partial dehydration of the original butyl alcohol. For the synthesis of the ester, hydrogen is not required.

The necessity for the presence of hydrogen in the reaction medium was especially apparent in the synthesis of methyl ethyl ketone from acetyl chloride and ethyl bromide. The ketonization reaction may be represented by the following scheme:



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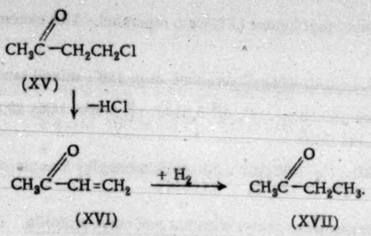

$$CH_3C(=O)-CH_2CH_2Cl \ (XV) \xrightarrow{-HCl} CH_3C(=O)-CH=CH_2 \ (XVI) \xrightarrow{+H_2} CH_3C(=O)-CH_2CH_3. \ (XVII)$$

Here, evidently, the final product should also be vinyl ketone (XVI). But, since vinyl ketone polymerizes very readily its isolation in considerable quantities is not feasible, and actually, it is present as traces in the reaction products. Methyl ethyl ketone is not formed unless hydrogen is supplied to the system. This is understandable, since hydrogen will not be formed from the acetyl chloride and ethyl bromide under the given conditions; therefore, in the absence of hydrogen, polymerization, resinification, and carbonization of the methyl vinyl ketone proceeds; no liquid reaction products form, and methyl ethyl ketone is not observed. If hydrogen is supplied to the system, then methyl ethyl ketone is formed in good yield.

For the purpose of a more accurate elucidation of the formation of methyl ethyl ketone from acetyl chloride and ethyl bromide in the presence of hydrogen, an experiment on the ketonization of a mixture of acetic acid and ethyl bromide was made, since it could be assumed that in the preceding experiment water formed in some way (on the basis of the oxygen in the acid chloride), and might have hydrolyzed the acid chloride or ethyl bromide. It was assumed that in the case of acetic acid and ethyl bromide, acetone would be obtained, since the reaction should proceed through the ester stages; thus the formation of methyl ethyl ketone was possible. The experiment showed that, from the acetic acid and ethyl bromide, only acetone formed; methyl ethyl ketone was not observed.

In the preceding experiment, if water had formed in some way so as to be free to hydrolyze the acetyl chloride and ethyl bromide, we should have obtained acetone and methyl ethyl ketone, but the latter was not observed.

Thus, these experiments showed that actually, a splitting off of the elements of the hydrogen halide from the alkyl halide molecule proceeds with simultaneous adsorption of the olefin onto the surface of the catalyst, and only after this does the interaction with acetyl chloride proceed. If a simultaneous splitting off of a chlorine atom and a bromine atom from both reacting molecules occurs, and their subsequent entry into the ketone molecule takes place, then the presence of an equimolecular quantity of hydrogen is not required for the reaction.

It is necessary to point out that, in the present investigation, the question of optimal conditions did not arise, since it was important to examine the new method and mechanism of the synthesis of ketones.

EXPERIMENTAL

Synthesis by Means of Acetic Acid and n-Butyl Alcohol

Preparation of the catalyst. The catalyst [3] in the amount of 52 g was applied to activated carbon, and then placed in a porcelain dish on a burner, and later was placed in a dark quartz catalytic tube.

Synthesis of ester. A mixture of acetic acid having a b.p. of 117° and n-butyl alcohol having a b.p. of 117°, in 1:1 volume ratio (100 ml), was passed over the catalyst at a rate of 25 ml per hour at 380-390°. The clear catalyzate (45 ml) obtained was separated into fractions: 1) 60-90°, 17 ml; 2) 90-110°, 12 ml; and 3) 110-121°, 12 ml. From the first fraction acetone was separated, and its 2,4-dinitrophenylhydrazone did not gave a depression with the known substance. The second fraction, appearing to be intermediate, contained acetone, water, acetic acid, and ester. The third fraction, together with the second, was treated with calcium chloride and diluted with a soda solution. After fractional distillation, approximately equal quantities of the butyl esters of acetic acid, (IV) and (V) were formed.

Sec-butyl ester (IV): b.p. 117°; d_4^{18} 0.8745; n_D^{18} 1.3881; MR_D 31.82, calculated 31.35.

n-Butyl ester (V): b.p. 124-126°; d_4^{18} 0.8862; n_D^{18} 1.3941; MR_D 31.34, calculated 31.35.

Synthesis of ketones. A mixture of acetic acid and n-butyl alcohol in a 1:1 volume ratio was passed over the catalyst at 475-485° at a rate of 15-18 ml per hour, in a quantity of 220 ml. The light-brown catalyzate (70 ml) obtained was treated with calcium chloride and distilled from a column. As a result, 35% of methyl sec-butyl ketone (X) and traces of methyl butyl ketone (XI) were separated. The excess of acetic acid was converted to acetone.

Acetone b.p. 57-65°; 2,4-dinitrophenylhydrazone m.p. 126°; mixed sample depression not given.

Methyl sec-butyl ketone (X): b.p. 118°; d_4^{18} 0.8100; n_D^{18} 1.399; MR_D 29.60, calculated 29.92; 2,4-dinitrophenylhydrazone m.p. 144-145°.

Methyl butyl ketone (XI): b.p. 125-127°; 2,4-dinitrophenylhydrazone m.p. 107°. Mixed sample depression not given.

Synthesis of ketones starting from acetyl chloride and ethyl bromide. A mixture of acetyl chloride and ethyl bromide in a 1:1 volume ratio (almost equimolecular) was passed over the catalyst (20 g), applied to asbestos wool. Previously, the catalyst tube had been treated with a current of hydrogen at 450° to remove water.

a) Experiment without hydrogen. We passed 50 ml of a mixture of acetyl chloride and ethyl bromide at 410-430° at a rate of 25 ml per hour. The catalyzate (7 ml) obtained consisted of 2.5 ml of ethyl bromide and 4 ml of acetyl chloride. No other products were separated. The catalyst was at once deactivated as a result of carbonization and deposition of resinous substances.

b) Experiment with hydrogen. We passed 50 ml of the same mixture at 410-430° at a rate of 15 ml per hour in the presence of hydrogen (the quantity, equimolecular content of C_2H_5Br). We obtained 20 ml of catalyzate, 70% of which consisted of methyl ethyl ketone, b.p. 80-82°; 2,4-dinitrophenylhydrazone m.p. 116-117°; no depression was given for mixed sample. Judging by the decolorization of bromine water, apparently methyl vinyl ketone was present in the form of traces. The bromine derivative, present in very small quantity, was not determined. The remaining 30% of the catalyzate consisted of unreacted initial products.

SUMMARY

1. The feasibility of the catalytic synthesis of esters and ketones from aliphatic alcohols and acids (acetic acid and n-butyl alcohol) over chrome-manganese catalysts was established, and a scheme was given for these reactions.

2. For the first time, the feasibility of catalytic synthesis of ketones from acid halides and alkyl halides (acetyl chloride and ethyl bromide) was established, and a scheme was given for the reaction.

3. It was shown that the initial stages of the mechanism of formation of esters and ketones from mixtures of acids and alcohols are analogous to the initial stages of formation of ketones from acid halides and alkyl halides.

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* See Consultants Bureau Translation, page 143.

CATALYTIC PRODUCTION OF MIXED KETONES FROM PRIMARY ALCOHOLS

I. KETONIZATION OF A MIXTURE OF ETHYL AND n-BUTYL ALCOHOL

B. N. Dolgov and G. V. Golodnikov

Recently, methods for obtaining ketones from primary alcohol shave been developed. The basis of this investigation was the work of Klyukvin and Ipatyev [1], who discovered acetone and methyl ethyl ketone in the cracking products of ethyl alcohol. In order to account for their formation, the authors proposed several schemes, and indicated the possibility of the intermediate formation of aldol.

Kagan, Podurovskaya, Klimenkov, Sobolev and Lubarsky studied the production of acetone from ethyl alcohol, using different catalysts [2-4], and proposed a reaction mechanism providing for the intermediate formation of aldehyde and ester:

$$\begin{array}{c} 4C_2H_5OH \rightarrow 4CH_3CHO + 4H_2 \\ 4CH_3CHO \rightarrow 2CH_3COOC_2H_5 \\ 2CH_3COOC_2H_5 \rightarrow CH_3COCH_3 + C_2H_4 + CO_2 + C_2H_5OH \\ \hline 3C_2H_5OH \rightarrow CH_3COCH_3 + C_2H_4 + CO_2 + 4H_2 \end{array}$$

The experimental data presented by the authors permit the conclusion that their scheme, analogous to that of Sabatier, seems to be extremely feasible. However, the reasons presented are clearly insufficient for complete clarification of the subsequent conversion: alcohol → aldehyde → ester → ketone.

In 1941-1946 Komarewsky, with his coworkers published a series of reports devoted to the production of ketones by passing the vapors of primary alcohols or their mixtures over chromium oxides at 400-450° [5-7]. The goundless attempt by these authors to represent these reactions as "new reactions" should be pointed out, since the given process was discovered and studied by Soviet chemists as early as 1932-1935. The aldol reaction mechanism that they propose also does not appear to be new – it was proposed in 1924 by Klyukvin and Ipatyev. The evidence for the aldol scheme is not sufficiently conclusive, since the proposed intermediate products (aldol and secondary alcohols) are not observed in the reaction products. Finally, the method proposed for obtaining the ketones is highly inconvenient, since the rate of carrying out the reaction should be very small (4-5 ml of alcohol per hour over 119 ml of catalyst, or a volume rate of 10-12).

Beginning with 1946, the ketonization reaction of primary alcohols was studied by the Department of Organic Chemistry of the Leningrad State University. B. N. Dolgov and B. A. Bolotov found and studied a series of very active copper catalysts, which permitted the reaction to be conducted at relatively low temperatures (275-375°) and at large volume rates (100-200) to obtain an extremely high yield of ketones (up to 80%) [8, 9]. The reaction was studied using primary alcohols of the normal and iso-structures having chain lengths of 2 to 6 carbon atoms. All the alcohols, except ethyl, give on ketonization only the corresponding symmetrical ketones, having 2n – 1 carbon atoms, where n is the number of carbon atoms in the molecule of the initial alcohol. From ethyl alcohol and acetone a mixture of ketones – methyl propyl ketone (up to 15% of the initial alcohol), and methyl amyl ketone, etc. – is obtained at 325-375°.

The formation of methyl propyl ketone supposedly proceeds according to the scheme:

$$CH_3COCH_3 + CH_3CHO \rightarrow [CH_3COCH_2CHOHCH_3] \xrightarrow[+\,H_2]{-H_2O} CH_3COCH_2CH_2CH_3.$$

Until now no method for obtaining mixed aliphatic ketones from mixtures of primary alcohols had been developed. We attempted to determine those conditions of reaction (temperature, time of contact, composition of the mixture, presence or absence of hydrogen, etc.), for which the chief product would be the mixed ketone, and for which the yield of symmetrical ketones would be reduced to a minimum. For carrying out the work we followed the ester scheme, in which the proposed intermediate products – aldehydes and esters – were invariably observed in the reaction products. The copper activated catalyst we used seems to have been the most effective of all the catalysts found by Dolgov and Bolotov during their study of the ketonization of individual primary alcohols [8].

TABLE 1

Temperature of the expts.	Yield (in % of the initial mixture)						
	acetone	methyl propyl ketone	dipropyl ketone	butyric aldehyde	ester	ethyl alcohol	butyl alcohol
1:1 molar							
275°	0.0	8.4	0.0	–	13.1	3.0	19.8
300	2.7	12.8	7.5	–	5.6	1.2	3.2
325	1.8	18.6	16.6	2.8	5.2	0.0	6.4
350	4.5	15.2	11.0	–	7.2	0.0	0.0
375	0.0	5.3	10.5	3.2	3.3	2.5	13.7
1:2 molar							
275	0.0	3.0	4.2	4.5	18.2	5.0	24.9
300	1.2	7.6	7.5	5.3	14.1	1.9	15.0
325	0.0	10.8	9.6	2.4	7.5	2.7	9.0
350	0.0	13.7	16.0	2.6	4.4	0.0	6.0
375	0.0	11.7	17.3	3.7	2.6	0.9	3.3
2:1 molar							
275	0.0	4.3	0.5	6.2	26.6	13.9	4.0
300	0.0	14.7	1.7	4.4	17.0	2.8	4.6
325	0.0	22.4	2.5	1.9	3.8	3.0	1.3
350	0.0	21.0	8.4	2.7	2.3	3.6	1.6
375	0.0	18.5	11.2	6.0	3.0	3.5	1.4
3:1 molar							
325	7.4	19.9	4.9	0.2	1.1	3.0	4.6
5:1 molar							
325	8.0	19.5	2.0	0.1	1.0	4.0	2.3

In the present article we consider experiments carried out using mixtures of ethyl and n-butyl alcohols, which were reacted in the presence of additional hydrogen added in 1:1 molar ratios to the alcohol mixture, since it was found that the addition of hydrogen increases the yield of ketones and promotes the preservation of the activity of the catalyst [8]. The conditions and results of the experiments are presented in Tables 1, 2 and 3.

It is evident from the data of Table 1 that the most favorable temperature for yields of the mixed ketone, methyl propyl ketone, is 325°, which is clear from the experiments using mixtures of ethyl and butyl alcohols in 1:1 molar ratios, carried out at uniform flow rates (volume rate of 150).

The largest yield of methyl propyl ketone was obtained at 2:1 molar proportions of ethyl and butyl alcohols (on further increase of the ethyl alcohol content in the mixture to 3 to 5 moles per mole of butyl alcohol, some decrease of the yield of methyl propyl ketone and the appearance of the symmetrical ketone, acetone, in the reaction products occurs). These experiments (Table 1) were carried out at different temperatures (from 275 to 375°) and at a constant volume rate (150).

From the results of the experiments using mixtures of alcohols in molar proportions of 2:1, it follows that the yield of ester decreases with an increase of temperature. For methyl propyl ketone there is a maximum at 325°, which corresponds to a minimum for butyric aldehyde. These data indicate the advantage of assuming the intermediate formation of aldehydes and esters during the formation of mixed ketones from alcohols.

As increase of the volume rate from 100 to 200 did not have any essential effect on the yields of methyl propyl ketone (Table 2), as is evident from the experiments using mixtures of ethyl and butyl alcohols (2:1 molar) at 325°. However, a further increase of the volume rate to 300 decreases the yield of methyl propyl ketone by a factor of 1.5. With a decrease of the time of contact, the quantity of butyric aldehyde and ester increases, since, apparently, the time of contact becomes insufficient for the further conversion of the aldehyde and ester.

TABLE 2

Volume rate	Yield (in % of the initial mixture)						
	acetone	methyl propyl ketone	dipropyl ketone	butyric aldehyde	ester	ethyl alcohol	butyl alcohol
57	1.6	17.8	7.2	0.9	1.7	4.3	0.0
98	0.6	22.0	7.0	1.4	4.4	3.0	1.7
152	0.0	22.4	2.5	1.9	3.8	3.0	1.3
198	0.8	19.6	6.5	4.8	10.4	4.2	3.6
300	2.3	14.4	3.3	7.8	12.8	6.3	10.0

TABLE 3

Conditions of experiment	Yield (in % of the initial mixture)						
	acetone	methyl propyl ketone	dipropyl ketone	butyric aldehyde	ester	ethyl alcohol	butyl alcohol
With added hydrogen.	0.6	22.0	7.0	1.4	4.4	3.0	1.7
Without hydrogen	1.4	18.1	0.0	2.3	9.9	6.6	6.0

TABLE 4.

Initial product	Yield (in % of the initial alcohols [mixture])						
	acetone	methyl propyl ketone	dipropyl ketone	butyric aldehyde	ester	ethyl alcohol	butyl alcohol
A mixture of ethyl and butyl alcohols (2:1 molar)	0.0	22.4	2.5	1.9	3.8	3.0	1.3
Ethyl alcohol . . .	9.7	12.5	—	—	0.8	13.0	—

For the purpose of investigating the effect of hydrogen, a mixture having a 2:1 molar composition was passed over a catalyst at 325°, at a volume rate of 100, i.e., under optimal conditions for producing the mixed ketone, but without simultaneous passage of hydrogen. From the data of Table 3 it is evident that in the absence of hydrogen a considerable decrease of the yield of methyl propyl ketone, and a decrease of the yield of dipropyl ketone to zero, are observed, and are accompanied by a parallel increase of the per cent of butyric aldehyde and, especially of the ester. This demonstrates the favorable action of hydrogen on the ketonization reactions.

Additional experiments were carried out using only one part of ethyl alcohol. From the data of Table 4 it is evident that from a mixture of ethyl and butyl alcohols (2:1 molar) almost twice as great a yield of methyl propyl ketone is obtained, as when only one part of ethyl alcohol is used. Consequently, on ketonization of a mixture of alcohols, the larger part of the methyl propyl ketone obtained forms because of the conversion of the molecules of both alcohols, and only a smaller part, possibly, is obtained as a result of the conversion of one part of ethyl alcohol.

EXPERIMENTAL

Apparatus and general method of procedure. The experiments were carried out employing the usual catalytic apparatus for investigating reactions in the heterogeneous phase. The initial mixture of alcohols was added gradually and continuously to the catalytic tube. The mixture of alcohols, condensed in the upper part of the tube, was passed into the catalyst. The reaction products passed through two coils, cooled by ice water. The liquid products were collected in receivers, but the gaseous products passed through two Tishchenko bottles containing a solution of hydroxylamine hydrochloride (for removing uncondensed aldehydes and ketones) and then passed into a graduated gasometer. Calculation of the rate of supply of the initial mixture of alcohols was made, starting from the known volume rate and from the calculation of the simultaneous passing of hydrogen. The temperature was controlled by means of a ferro-constantan thermocouple. At the beginning of each experiment the first portion of condensate and gas was rejected. Usually only after 30 minutes, when equilibrium of the supplied mixture was established, and the temperature was indicated accurately, did we begin the reading and recording of the liquid and gaseous products.

Analysis of the reaction products. The acidity and total ester content were determined on a sample of catalyzate from each experiment. Further catalyzates were fractionated, using a Todd type fractionating column having an efficiency of 25 theoretical plates. The fractions obtained were analyzed for their contents of ketones, aldehydes and esters. Determination of the aldehydes was carried out by the ammoniacal silver method. The ketone content was determined, after a preliminary test for aldehydes, by the hydroxylamine method. In the case of simultaneous presence of ketones and aldehydes in a fraction, the aldehydes were determined as usual by the ammoniacal silver method, and the sum of aldehydes and ketones was determined by the hydroxylamine method; the ketone content was then determined by difference. The ester content was determined by saponification of a neutralized weighed portion of sample using a 0.1 N alcoholic solution of KOH, and back-titrating the excess alkali with 0.1 N HCl. Calculations were made for the ester, corresponding to the boiling point of the given fraction. When two or three esters were present in a fraction, the calculation was made for the ester having the lowest molecular weight. The fractional distillations and analyses of the fractions served as a basis for calculation of the yields of the reaction products.

During all the experiments, the quantity of gas liberated was measured. Gas analyses were made using a gas analyzer of the VTI system.

Ketonization of a mixture of ethyl and n-butyl alcohols. For the work we used commercial ethyl alcohol – fractionally distilled (95%), d^{18} 0.805, and n-butyl alcohol, which after drying over Na_2SO_4 and distilling, had a b.p. of 116.5-118.0°; d^{18} 0.806 and n_D^{18} 1.3997.

The liquid condensate from each experiment was fractionated. Usually on fractionation, the following fractions were obtained: 1) 54-60°, 2) 60-80°, 3) 80-100°, 4) 100-105°, 5) 105-118°, 6) 119-130°, 7) 130-140°, 8) 140-146°, and 9) 146-170°; residue (above 170°). The fractions, from all the distillations, which had identical boiling points were combined, after being analyzed for their ketone, aldehyde and ester contents, and fractionally distilled for the purpose of separating the individual substances and identifying them.

The first fraction contained acetone, which was separated and identified:

B.p. 56.0-56.3°; n_D^{20} 1.3589; d_4^{20} 0.7916.

Literature data: b.p. 56°; n_D^{20} 1.3590; d_4^{20} 0.7912. p-Nitrophenylhydrazone: m.p. 148.0-148.5° (in literature 148-149°).

Found %: N 21.90. $C_9H_{11}O_2N_3$. Calculated %: N 21.76.

The second fraction contained ethyl acetate, which was determined by saponification; butyric aldehyde, which was determined by the ammoniacal silver method; and ethyl alcohol, the content of which was calculated by difference.

In the third fraction the content of butyric aldehyde was also determined by the ammoniacal silver method; methyl propyl ketone was calculated by difference using the hydroxylamine method.

The fourth fraction represented almost pure methyl propyl ketone, which was isolated and identified:

B.p. 101.8-102.7°; n_D^{20} 1.3902; d_4^{20} 0.8090.

Literature data: b.p. 102.3°; n_D^{20} 1.39012; d_4^{20} 0.80639.

Found: M 85.0, 84.5. $C_5H_{10}O$. Calculated: M 86.

The semicarbazone after three recrystallizations had a m.p. of 111-112° (in the literature 112°).

Found %: N 29.60. $C_6H_{13}ON_3$. Calculated %: N 29.37.

The fifth fraction consisted chiefly of unreacted butyl alcohol; it also contained some methyl propyl ketone.

The sixth fraction contained not more than 2-3% by weight of condensates and, according to the analysis, contained esters, probably ethyl butyrate (b.p. 121.6°) and butyl acetate (b.p. 126.2°), but it was not investigated carefully.

The seventh fraction, appearing to be intermediate, contained no more than 4-5% by weight of condensates, and contained some dipropyl ketone.

The eighth fraction represented almost pure dipropyl ketone which, by repeated fractionation, was separated and identified:

B.p. 143-144°; n_D^{20} 1.4075; d_4^{20} 0.8170.

Literature data: b.p. 144.1°; n_D^{20} 1.40732; d_4^{20} 0.8175.

Found: M 112.8, 114.0. $C_7H_{14}O$. Calculated: M 114.

The semicarbazone after two recrystallizations had a m.p. of 133.5-134.0° (in literature 133°).

Found %: N 24.89. $C_8H_{17}ON_3$. Calculated %: N 24.56.

The ninth fraction contained butyl butyrate, which was isolated by repeated fractional distillation and identified:

B.p. 165.0-166.5°; n_D^{20} 1.4073; d_4^{20} 0.8700.

Literature data: b.p. 166.7°; n_D^{15} 1.4087; d_4^{15} 0.8712.

Found: M 140.2, 142.1. $C_8H_{16}O_2$. Calculated: M 144.

Saponification of the fraction by 25% KOH gave butyric acid, which was further converted to the silver salt.

Found %: Ag 55.41. C_3H_7COOAg. Calculated %: Ag 55.36.

The residue (above 170°) contained, according to analysis, ketones and esters. Further study of the residue was not undertaken.

The compositions of the gases from the experiments, optimal for yields of mixed ketone, were characterized by considerable contents of H_2 (80-85%), CO_2 (6-7%) and CO (5-6%). Olefins and saturated hydrocarbons were present in negligible amounts.

SUMMARY

1. The advantageous formation of methyl propyl ketone over activated copper catalyst was observed using mixtures of ethyl and n-butyl alcohols in 2:1, 3:1 and 5:1 molar proportions at a temperature of 325° and at a volume rate of 100-200. Under these conditions the yields of methyl propyl ketone amounted to 20-22% of the initial mixture of alcohols; the symmetrical ketones formed in small amounts (acetone 0-8%, dipropyl ketone 3-8%). The sum of the yields of the ketones amounted to 30-32% of the initial mixture.

2. At low temperatures, esters were obtained in good yield (to 26%). Ethyl acetate and butyl butyrate were found in the reaction products. Probably, also ethyl butyrate and butyl acetate formed in small amounts.

3. An examination of the relationship of the yields of aldehydes and esters to changes of temperature and times of contact, confirmed the assumption that aldehydes and esters appear as intermediate products during the formation of methyl propyl ketone from a mixture of alcohols.

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CATALYTIC REDUCTION OF NITROBENZENE DURING ITS REACTION WITH HYDROCARBONS AND ALCOHOLS

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The literature data on the reaction of nitrobenzene with the paraffin hydrocarbons or alcohols is very limited. Reactions were described in which nitrobenzene and p-nitrotoluene reacted with ethane in the presence of the chromites of nickel, cobalt and cadmium at 400°, leading to production of aniline and p-toluidine [1]. On heating nitrobenzene with isopropyl [2] or benzyl alcohol [3] at 100-140° in the presence of caustic soda, there was oxidation of the alcohols with the formation of acetone and benzoic acid, and reduction of the nitrobenzene, in the first case to aniline, and in the second to azobenzene. On boiling a mixture of benzyl alcohol, aniline and nitrobenzene in the presence of aluminum oxide, the alcohol was quantitatively oxidized to benzaldehyde, which with aniline gave azomethine compounds [4].

In the present work, the reaction of nitrobenzene with n-butane, and mixtures of butenes and n-butyl alcohol in the presence of chromic oxide on aluminum oxide was studied. It was found that at 550° the mixture of nitrobenzene with n-butane and with mixtures of butenes gave catalyzates from which, besides unaltered nitrobenzene (10-8%), aniline and diphenyl (yield 10-5% and correspondingly (5.5-6% on the basis of nitrobenzene), and also small quantities of naphthalene were obtained. The reaction was accompanied by strong decomposition with the formation of carbon dioxide and carbon monoxide, ammonia, water, hydrogen, gaseous unsaturated (ethylene and propylene) and saturated hydrocarbons, resins and carbonaceous material.

At 450° a mixture of butenes with nitrobenzene gave aniline (yield 8%), traces of diphenyl and unaltered nitrobenzene (37%).

In the absence of a catalyst, at 440° a mixture of nitrobenzene with n-butane gave aniline (yield 4%), diphenyl (yield 5.5%) and unaltered nitrobenzene (17%).

The reaction of n-butyl alcohol with nitrobenzene in the presence of chromic oxide on aluminum oxide at 450° led to the production of aniline (yield 33%) and diphenyl (yield 2%); the catalyzate also contained unaltered nitrobenzene (27%) and alcohol (12.5%).

In none of the reaction products were traces of the pyrrole compounds observed.

In the literature there was no information on the formation of diphenyl from nitrobenzene or aniline. It was reported that, on heating above 356° in an atmosphere of hydrogen, nitrobenzene decomposes explosively, giving a carbonaceous material; on addition of aniline, resin-like substances form [5]. If aniline vapors are passed through an incandenscent tube, decomposition products not containing diphenyl are formed [6-10]. On passing aniline over aluminum oxide at 500°, a small yield of diphenyl is produced; the yield of the latter is increased considerably if there is previous contact with hydrochloric acid during the process [11]. In an atmosphere of hydrogen the chief reaction products are benzene (23%) and ammonia, since only traces of diphenyl form [12].

In our experiments the reaction took place in an atmosphere of hydrogen (the gaseous reaction products contained 6-15% of hydrogen), because the formation of diphenyl can be expected as a result of the reduction of nitrobenzene to aniline, the splitting off of the ammonia part of the aniline molecule with formation of the phenyl radical, and stabilization of the latter by forming diphenyl (in the presence of an oxidizing agent the addition of hydrogen and formation of benzene from nitrobenzene was prevented).

$$2C_6H_5NH_2 + H_2 \xrightarrow[Cr_2O_3/Al_2O_3]{(C_6H_5NO_2)} C_6H_5-C_6H_5 + 2NH_3.$$

EXPERIMENTAL

The starting materials were: a) a mixture of butenes, obtained by dehydration of n-butyl alcohol over

Cr_2O_3/Al_2O_3:* b) n-butane, containing (in %): olefins 2.3, CO_2 0.2, CO 1.5, O_2 1.0 and H_2 0.4 (all calculations of yields refer to 94.6% n-butane); c) n-butyl alcohol: b.p. 115-116° (747 mm); n_D^{20} 1.3983; d_4^{20} 0.8108; d) nitrobenzene: b.p. 85-86° (10 mm); n_D^{20} 1.5524; d_4^{20} 1.2033.

Chromic oxide on aluminum oxide (20% chromic oxide) produced a mixed aqueous solution of chromic anhydride and aluminum oxides [13]; dried at 110°, it was placed in a tube having an inside diameter of 13 mm [34 g (50 ml) of catalyst] and dried further in a current of air at 450°.

Below we present some typical experiments from each series.

Reaction of n-Butane and Nitrobenzene

a) Nitrobenzene was introduced over a catalyst in a current of n-butane, the rate of introduction being measured by a rheometer. A mixture of 35.5 g (0.29 mole) of nitrobenzene and 15.0 g (0.27 mole) of n-butane (1.1:1) was passed over a catalyst at 550° for 60 minutes; the volumetric rate of introduction of butane was 0.5 ml of liquid butane/ml of catalyst per hour. The container was cooled with a mixture of ice and salt. The gaseous reaction products were passed into 2 wash bottles containing acetic acid (for absorption of ammonia), and then were collected in a gasometer over a saturated salt solution.

The catalyzate (15 g of an oily layer and 5 g of an aqueous layer) was shaken with a dilute solution of hydrochloric acid and extracted with petroleum ether (b.p. 35-45°). Then the hydrochloric acid solution was alkalinzed and extracted with ethyl ether. In this way 2 extracts were obtained, (I) containing neutral reaction products and (II) containing basic reaction products, — and these were dried over calcined potash.

I. The residue (5.6 g) obtained after elimination of the petroleum ether, did not distill even on heating to 150°; this indicated the absence of benzene in the neutral reaction products. The following fractions were separated by distillation in vacuo at 3 mm:

First fraction, b.p. 58-61°, n_D^{20} 1.5443 — 0.6 g; second fraction, b.p. 61-62°, n_D^{20} 1.5540 — 2.1 g; third fraction, b.p. 62-75°, n_D^{20} 1.5630 — 0.8 g; fourth fraction, b.p. 75-92°, — 0.1 g; fifth fraction, b.p. 92° — 0.7 g; resinous material — 0.9 g.

The second fraction represented unaltered nitrobenzene (6% of the original). From the third fraction, frozen, we separated 0.1 g of naphthalene having a m.p. of 79.5-80°; for the sample mixed with a known amount of naphthalene no m.p. depression was observed. The fifth fraction was identified as diphenyl: m.p. 69.5° (from methyl alcohol); no m.p. depression was observed on mixing the sample with known diphenyl. The yield, based on nitrobenzene, was 3%.

II. The residue (3.6 g) obtained after elimination of the ether, by distillation at 50-51° (3 mm), had n_D^{20} 1.5861 and represented aniline (2.7 g, yield 10%); its acetyl derivative melted at 113.5°, and a sample mixed with known acetanilide gave no m.p. depression.

III. The increase in weight of the wash bottles containing acetic acid (2.0 g) indicated the formation of ammonia during the reaction.

TABLE

Fraction No.	Boiling point at 60 mm	Quantity (g)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
1st	57-59°	3.3	1.5370	2.1811	26.90	26.96
2nd	59-64	3.3	1.5270	2.0156	—	—
3rd	64-66	6.6	1.5219	1.9336	31.84	31.58

The gases, collected in the gasometer (6420 ml S.T.P.), contained (in %): CO_2 23.3, CO 21.6, O_2 0.6, H_2 5.5, C_nH_{2n} 20.6, C_nH_{2n+2} 28.4.

In two other such experiments the gases were passed through a wash bottle containing bromine, and 22.6 g of bromides was obtained. The following fractions were obtained from them by fractional distillation: (see Table).

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* Study of the Raman spectrum of the dibromides obtained from this mixture of butenes showed that ~20% of butene-1 and ~80% of butene-2 enter into its composition.

The first fraction represented 1,2-dibromoethane, the third, 1,2-dibromopropane, the second fraction was a mixture of both dibromides. Thus, ethylene and proplyene were found in the gaseous reaction products.

Literature data: 1,2-dibromoethane, b.p. 57.9° (60 mm) [14]; b.p. 130.5° (758 mm), n_D^{20} 1.53891, d_4^{20} 2.1829 [15]; 1,2-dibromopropane, b.p. 66.4° (60 mm) [14]; b.p. 141.5° (770 mm), n_D^{20} 1.52006, d_4^{20} 1.9324 [15].

b) A mixture of 17.8 g (0.15 mole) of nitrobenzene and 6.7 g (0.12 mole) of butane (1.2:1) was passed through a purification tube at 550° for 60 minutes. The catalyzate (14 g), containing very little water, was subjected to the treatment described above, as a result of which was obtained: aniline 0.5 g [b.p. 50-51° (3 mm), n_D^{20} 1.5865, yield 3.5%], diphenyl 0.6 g (m.p. 69.5°, yield 5.5%), unaltered nitrobenzene 1.8 g [b.p. 61-62° (3 mm), n_D^{20} 1.5518, d_4^{20} 1.2022, yield 10%].

Reaction of a Mixture of Butenes with Nitrobenzene

A mixture of 54.0 g (0.44 mole) of nitrobenzene and 16.2 g (0.29 mole) of a mixture of butenes (1.5:1) was passed over a catalyst at 550° for 65 minutes; the volumetric rate of passage of the mixture of butenes was 0.45. The catalyzate (24 g of oily layer and 4 g of aqueous layer) was extracted with ether; then the ether layer was dried over calcined potash. After elimination of the ether, the product did not give any distillate even on heating to 150°; but by distillation in vacuo, 2 fractions were separated: the first was liquid (9.5 g), boiling at 75 to 90° (13 mm), and the second was a crystallizing (2.5 g) fraction converted at 110-125° (13 mm), from which 2.0 g (6%) of diphenyl having a m.p. of 69.5° was separated by recrystallization from methyl alcohol; no m.p. depression was observed when the sample was mixed with known diphenyl.

The first fraction (75-90°) was treated with dilute hydrochloric acid, and then extracted with petroleum ether (b.p. 35-45°).

I. After elimination of the petroleum ether from the residue of the extract dried over calcined potash (6.1 g of neutral reaction product), the residue was distilled in vacuo and gave 0.9 g of a fraction having a b.p. of 61-63° (3 mm) and n_D^{20} 1.5547, 4.1 g of a fraction having a b.p. of 63° (3 mm) and n_D^{20} 1.5615, and 0.8 g of resinous substance. By freezing the second fraction, 0.2 g of naphthalene having a m.p. of 79.5-80° was obtained; no m.p. depression was observed when the sample was mixed with known naphthalene. Thus, the first and second fractions represented a mixture of unaltered nitrobenzene (yield 8%) with naphthalene.

II. The hydrochloric acid solution was alkalinized and extracted with ethyl ether. After elimination of the ether and distillation of the residue (2.6 g) 2.0 g of aniline (yield 5%), b.p. 50-52° (3 mm) and n_D^{20} 1.5851 was obtained; its acetyl derivative melted at 113.5°, and the sample when mixed with known acetanilide produced no m.p. depression.

Reaction of n-Butyl Alcohol with Nitrobenzene

A mixture of 37.0 g (0.30 mole) of nitrobenzene and 22.2 g (0.30 mole) of n-butyl alcohol (1:1) was passed over a catalyst at 450° for 60 minutes; the volumetric rate of introduction of the alcohol was 0.55. The exit gases were passed through wash bottles containing acetic acid, 30% solution of caustic potash, bromine and a solution of caustic potash.

The catalyzate (42 g) containing 7 g of aqueous layer and poorly separated, was treated just as in the experiment with n-butane.

I. From the part of the catalyzate (16.9 g) which was insoluble in hydrochloric acid solution, the following fractions were obtained by distillation in vacuo: first, b.p. 59° (55 mm), n_D^{20} 1.4156 – 2.8 g; second, b.p. 54-56° (2 mm), n_D^{20} 1.5548, d_4^{20} 1.2028 – 9.9 g; third, b.p. 104-108° (2 mm) – 1.2 g; fourth, b.p. 108-150° (2 mm) – 1.4 g; resinous substance 1.2 g.

The first fraction represented unaltered alcohol (12.5%), containing a mixture of nitrobenzene. n-Butyl-3,5-dinitrobenzoate, obtained by reaction of 3,5-dinitrobenzoyl chloride, melts at 62.0-62.5°; no m.p. depression was observed when the sample was mixed with known n-butyl-3,5-dinitrobenzoate.*

The second fraction represented unaltered nitrobenzene (27%). The third fraction, on dilution with a small amount of methyl alcohol and cooling with dry ice, gave 0.5 g of diphenyl (yield 2%), having a m.p. of 69.5°; no m.p. depression was observed when the sample was mixed with known diphenyl. The fourth fraction was not closely studied.

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* Literature data for n-butyl-3,5-dinitrobenzoate [16]: m.p. 62.5°.

II. From the part of the catalyzate (11.0 g) which was soluble in hydrochloric acid solution, 9.3 g of aniline (yield 33%): b.p. 54-55° (4 mm), n_D^{20} 1.5852, was separated; its acetyl derivative melted at 113.5° and the sample when mixed with known acetanilide showed no m.p. depression.

III. For the wash bottles containing acetic acid the gain in weight was 0.7 g (ammonia); for the bottles containing alkali it was 2.3 g (carbon dioxide). The mixture of dibromides (10.5 g) obtained by distillation in an interval of 130-149° (747 mm), as in the case described above, represented a mixture of 1,2-dibromoethane and 1,2-dibromopropane. 1,2- and 2,3-dibromobutane, having higher boiling points: 160.3° (760 mm) [17] and 157-159° (760 mm) [18], might be present here only as mixture.

In the other experiments, the gases were passed through only a wash bottle containing acetic acid, and were then collected in a gasometer. We collected 5910 ml (S.T.P.) of gas, containing (in %): CO_2 19.3, CO 34.0, H_2 15.2, O_2 0.2, C_nH_{2n} 18.2, C_nH_{2n+2} 13.1. A large amount of the carbon monoxide can be accounted for by oxidation of the alcohol to n-butyraldehyde and decomposition of the latter to carbon monoxide and propane.

SUMMARY

1. By reaction of nitrobenzene with n-butane and with mixtures of butenes at 450-550°, and also with n-butyl alcohol at 450° in the presence of chromic oxide on aluminum oxide, part of the nitrobenzene was reduced to aniline (to 33%), and part of it remained in the unaltered form (to 37%).

2. The formation of diphenyl (to 6%) observed in all cases, depended on the splitting off of ammonia from aniline, which occurred on reaction with hydrogen in the presence of an oxidizing agent – nitrobenzene. In the presence of nitrobenzene the addition of hydrogen to the phenyl radical, leading to benzene, is inhibited and only the stabilization of diphenyl proceeds.

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INVESTIGATION OF THE TRANSFORMATION OF PINACOLS WITH SUBSTITUTED ACETYLENIC RADICALS

X. SYNTHESIS AND TRANSFORMATION OF SYMMETRICAL DIMETHYLPHENYLPHENYLACETYLENEETHYLENE GLYCOL

(3-METHYL-2,5-DIPHENYLPENTYNE-4-DIOL-2,3)

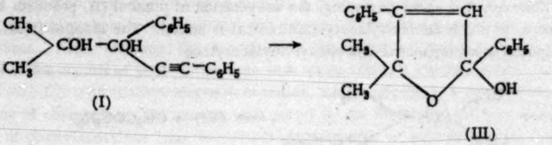
E. D. Venus-Danilov and V. I. Serkov

In connection with the study of the transformation of di-tertiary α-glycols of the acetylene series [1-8], great interest is attached to the synthesis of symmetrical dimethylphenylphenylacetyleneethylene glycol (II) (3-methyl-2,5-diphenylpentyne-4-diol-2,3), an isomer of the asymmetrical dimethylphenylphenylacetyleneethylene glycol (I) (2-methyl-3,5-diphenylpentyne-4-diol-2,3) studied earlier by one of us [1].

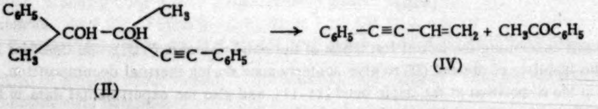
It was explained that the properties and transformations of these two pinacols, which differ only in the position of the methyl and phenyl groups on the hydroxyl-bearing carbon atoms, are extremely different.

Pinacol (I) represents an excellently crystallizing substance having a m. p. of 93-93.5° [1], which on heating with 30% sulfuric acid isomerizes, by a type of acetylene-allenic rearrangement [9], to 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (III).

Pinacol (II) easily undergoes thermal decomposition; on reaction with sulfuric acid it brings about neither acetylene-allenic nor pinacolinic rearrangement, but the cleavage of pinacol with the formation of phenylvinylacetylene (IV) and acetophenone is observed.



(I) (III)



(II) (IV)

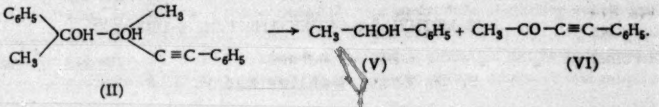
We obtained 3-methyl-2,5-diphenylpentyne-4-diol-2,3 from phenylacetylene and methylphenylacetylcarbinol by the Iotsich method. The carbinol was prepared from diacetyl and phenyl magnesium bromide. It is interesting that the attempt to introduce the phenylacetylene radical into the diacetyl at first, and later into the acetylenic ketoalcohol (3-methyl-5-phenylpentyn-4-ol-3-one-2) was not successful; the acetylenic ketoalcohol [10] was produced in good yield, but did not react with the phenyl magnesium bromide.

The synthesized symmetrical dimethylphenylphenylacetyleneethylene glycol (II) was carefully purified of the contaminant, phenylacetylene, and took the form of a viscous, transparent, slightly tinted mass, not crystallizing over long periods of standing. It is possible that the crystallization is inhibited by the presence of the two diastereoisomeric forms — the symmetrical methyldiphenylphenylacetyleneethylene glycol [5], which does not crystallize during long periods of storage, and symmetrical methyldiphenyltertiarybutylacetyleneethylene glycol [6] which crystallizes only after 1.5 years.

The pinacol was of sufficient purity, since the analytical data for it were satisfactory.

During an attempt to distill pinacol in vacuo, it decomposed, whereby about 40% of the methylphenylcarbinol (V) was separated, and it was contaminated by mixtures of a small amount of carbonyl compounds, some diphenyl and considerable quantities of resin, but no acetophenone was observed.

Taking into account the products of the thermal decomposition of pinacol (II), it should be pointed out that, in contrast to the previously observed thermal decomposition of pinacols of the acetylenic series [5, 6] forming acetophenone and an alcohol of the acetylenic series, we obtained a different arrangement of hydrogen atoms – forming methylphenylcarbinol (V) and, apparently, negligible amounts of a ketone of the acetylenic series (VI):



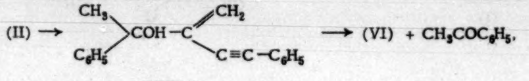
$$\longrightarrow CH_3{-}CHOH{-}C_6H_5 + CH_3{-}CO{-}C{\equiv}C{-}C_6H_5.$$

The cleavage of pinacol is different when it reacts with sulfuric acid. On heating pinacol (II) with 30% sulfuric acid we obtained acetophenone and phenylvinylacetylene (IV), the structure of which was demonstrated by its ozonolysis with the formation of benzoic, oxalic and formic acids. The properties of the hydrocarbon obtained are analogous to the properties of the vinylalkylacetylene, $R{-}C{\equiv}C{-}CH{=}CH_2$, described by Petrov and Leporskaya [11] and foreign chemists [12, 13]. Similar to this substance, phenylvinylacetylene shows an increase of its molecular refraction and does not polymerize on standing.

The question concerning the formation of this hydrocarbon deserves attention. Phenylvinylacetylene (IV) may be formed from symmetrical dimethylphenylphenylacetyleneethylene glycol (II), as a result of its ketonic decomposition forming acetophenone and a secondary acetylenic alcohol – methylphenylacetylenecarbinol (VII), which on dehydration in acid medium forms the hydrocarbon (IV):

$$\text{(II)} \rightarrow CH_3{-}CO{-}C_6H_5 + \underset{\text{(VII)}}{CH_3{-}CHOH{-}C{\equiv}C{-}C_6H_5} \rightarrow \text{(IV)}.$$

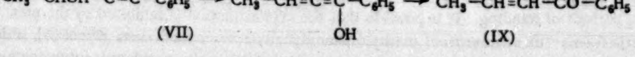
It is more probable, however, that at the beginning, the dehydration of pinacol (II) proceeds because of the hydrogen of the methyl groups, to which the phenylacetylenic radical is joined. The alcohol (VIII) forming in this case may be further decomposed to acetophenone and phenylvinylacetylene:



(VIII)

On the hypothesis concerning the initial formation of the eninic alcohol (VIII): we consider it plausible, taking into account the inability of pinacol (II) to give acetophenone during thermal decomposition, the large mobility of the hydroxyl in the α-position at the triple bond [14-17], and also the experimental data of Favorskaya and Zakharyevskaya [18] from the study of the transformation of symmetrical dimethylisobutylacetyleneethylene glycol.

In order to explain the mechanism of the formation of phenylvinylacetylene and to confirm the assumption of the primary formation of the eninic alcohol, we explored the action of 30% sulfuric acid on methylphenylacetylenecarbinol* (VII) on heating. Thus, ethylideneacetophenone (IX), and not phenylvinylacetylene (IV) was formed. The obtainment of ethylideneacetophenone may be explained by the acetylene-allenic rearrangement of the methylphenylacetylenecarbinol through the enol form of this ketone:



$$\underset{\text{(VII)}}{CH_3{-}CHOH{-}C{\equiv}C{-}C_6H_5} \rightarrow CH_3{-}CH{=}C{=}\underset{\substack{| \\ OH}}{C}{-}C_6H_5 \rightarrow \underset{\text{(IX)}}{CH_3{-}CH{=}CH{-}CO{-}C_6H_5}$$

Similar isomerization of the acetylenic alcohols has been sporadically described in the literature [19-22]. Consequently, methylphenylacetylenecarbinol is not dehydrated by the action of 30% sulfuric acid, which refutes our first assumption concerning the order of formation of acetophenone from methylphenylacetylenecarbinol (VII).

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* The methylphenylacetylenecarbinol was given to us by L. A. Pavlov, to whom we express our thanks.

Phenylvinylacetylene, together with acetophenone, forms during the ketonic transformation of the eninic alcohol (VIII) – a product of the dehydration of pinacol (II).

The work showed that symmetrical dimethylphenylphenylacetyleneethylene glycol (II), on the action of sulfuric acid, does not form ethylenic γ -ketoalcohol or its cyclization product – substituted hydroxydihydrofuran, as occurred for some of the pinacols that we studied earlier [1, 2, 3, 5]. For this pinacol we did not observe a pinacolinic transformation, which might be expected by analogy with the other pinacols of this series [4-8]. The only transformation of symmetrical dimethylphenylphenylacetyleneethylene glycol by the action of 30% sulfuric acid seems to be dehydration with subsequent ketonic decomposition. It is possible that under more mild reaction conditions, eninic alcohol (VIII) or other products might be obtained.

Consideration of the properties and transformations of 3-methyl-2,5-diphenylpentyne-4-diol-2,3-(II) again emphasizes clearly that the stability of the acetylenic pinacol molecules, and their transformations, depends on the mutual intramolecular phenomena of the radicals, and on their arrangement in the molecules.

EXPERIMENTAL

I. Production of 3-Methyl-2,5-diphenylpentyne-4-diol-2,3 (Symmetrical Dimethylphenylphenylacetyleneethylene Glycol)

Pinacol was synthesized from methylphenylacetylcarbinol and phenylacetylene magnesium bromide.

The most convenient method of obtaining methylphenylacetylcarbinol was by the reaction of diacetyl (1 mole) with phenyl magnesium bromide (1 mole). The yield was 35%:

B.p. 93-95° (5 mm); semicarbazone: m.p. 181°. Literature data: b.p. 126-127° (12 mm); semicarbazone: m.p. 182-183° [23-24].

The melting point of a mixture of the semicarbazone obtained with the known semicarbazone showed no m.p. depression.

Several experiments on the production of symmetrical dimethylphenylphenylacetyleneethylene glycol (II) were carried out, and they gave similar results. We present one of the experiments. Into phenylacetylene magnesium bromide, obtained from 6 g of magnesium, 27 g of ethyl bromide, and 26 g of phenylacetylene, an ether solution of 21 g of methylphenylacetylcarbinol was poured. The reaction proceeded quietly with external cooling with cold water. After the usual decomposition of the magnesium complex, recovery of the reaction product and elimination of the excess of phenylacetylene with water vapor, a viscous, yellow mass was obtained, and it gave a positive reaction with methyl magnesium iodide, and decolorized an aqueous solution of potassium permanganate and bromine in chloroform. On heating with potash by the method of Babayan [25] at 185°, decomposition with separation of phenylacetylene (the precipitate obtained with an ammoniacal solution of silver okide) began.

0.1196 g sub.: 0.3552 g CO_2; 0.0779 g H_2O. 0.0550 g sub.: 9.7 ml CH_4 (21°, 758 mm). 0.1618 g sub.: 11.53 g benzene: Δt 0.27°. Found %: C 81.03; H 7.23; OH 12.3; number of OH-groups 1.9; M 261. $C_{18}H_{18}O_2$. Calculated %: C 81.20; H 6.77; OH 12.7; number of OH-groups 2.0; M 266.

On distillation of pinacol under vacuum it decomposed, beginning at a bath temperature of about 140°. The following fractions were obtained:

First fraction, b.p. at 84° (3 mm), several drops; second fraction, b.p. 84-87° (3 mm), 36% of the initial quantity; third fraction, b.p. 100-110° (3 mm), a small quantity of liquid and solid substances; residue – resin, 42% of the initial substance.

The first fraction did not produce a turbidity with a solution of 2,4-dinitrophenylhydrazine; the third corresponded to diphenyl, with m.p. of 62° (mixed sample); the second fraction on redistillation boiled at 84-85° (3 mm), (n_D^{20} 1.5362) and gave very little of the higher boiling substance.

9.16 mg sub.: 2.63 mg CO_2; 0.71 mg H_2O. 0.0500 g sub.: 8 ml CH_4 (13°, 774 mm). 0.1622 g sub.: 12.21 g benzene: Δt 0.45°. Found %: C 78.62; H 8.61; OH 11.6; number of OH-groups 0.82; M 147. $C_8H_{10}O$. Calculated %: C 78.70; H 8.20; OH 13.8; number of OH-groups 1; M 122.

According to the literature data for methylphenylcarbinol [26]: b.p. 85° (5 mm), n_D^{20} 1.5211.

The substance reacted energetically with methyl magnesium iodide, but not especially rapidly with an aqueous solution of potassium permanganate and with bromine in chloroform.

On standing with a solution of 2,4-dinitrophenylhydrazine, a very small precipitate separated (especially from the fraction boiling above 85° at 3 mm, on redistillation). Because of the small quantity of this substance, its purification was not successful; in determining the m.p., we observed decomposition at 210°.

During decomposition of the substance under vacuum, acetophenone was not observed from the reaction with 2,4-dinitrophenylhydrazine either in the first fraction having a boiling point of up to 84° (3 mm), or on redistillation of the product.

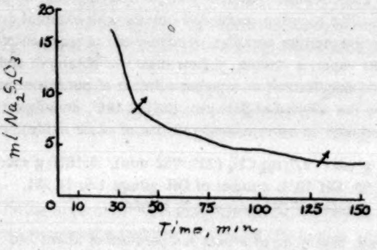
Oxidation of the substance having a boiling point of 84-85° at 3 mm by chromic anhydride. Into a solution of 2.5 g of the substance in 25 ml of glacial acetic acid, a solution of 1.2 g of chromic anhydride in 25 ml of glacial acetic acid was poured. The mixture was heated to 60°, with stirring, for 1.5 hours. The greenish-brown solution was diluted with water, neutralized with soda, and steam distilled. Ether extraction was used for recovery of the neutral oxidation products, which were volatile with the vapor. After removal of the ether, a colorless, strongly refractive liquid (b.p. 68° at 6 mm, n_D^{25} 1.5315) having the odor of acetophenone, was obtained; it did not react with methyl magnesium iodide at all, but gave a voluminous orange-yellow precipitate with 2,4-dinitrophenylhydrazine. The melting point of the 2,4-dinitrophenylhydrazone was 238° with decomposition. The semicarbazone having a m.p. of 200° formed from semicarbazide. The 2,4-dinitrophenylhydrazone and the semicarbazone did not produce a reduction of the melting points with known 2,4-dinitrophenylhydrazone and the known semicarbazone of acetophenone.

The literature data for acetophenone [27]: b.p. 64° at 5 mm; n_D^{19} 1.5338; 2,4-dinitrophenylhydrazone [28]: m.p. 250°; semicarbazone [28]: m.p. 198°.

According to the analytical data, the oxidation product did not correspond completely to pure acetophenone.

II. Action of 30% Sulfuric Acid on 3-Methyl-2,5-diphenylpentyne-4-diol-2,3

We heated 20 g of pinacol to weak boiling, stirring strongly, with 200 ml of 30% sulfuric acid for 2 hours. From the acid solution, 18 g of a dark substance having a pungent odor was extracted by ether. The ether extract from the neutralized solution contained no products.



Curve for ozonization of phenylvinylacetylene Concentration of O_3 in ml of $Na_2S_2O_3$ per 18.5 ml entering. TO_3 0.00230 g/ml.

The substance obtained boiled at 64-66° (4 mm); at elevated temperatures, distillation was accompanied by strong decomposition, and in the residue there was a considerable quantity of a resinous substance.

The substance instantly decolorized an aqueous solution of potassium permanganate, reacted violently with bromine, but gave no reaction with the hydroxyl group. With a solution of 2,4-dinitrophenylhydrazine a small precipitate having a decomposition temperature of 232° was obtained, and its mixture with the known 2,4-dinitrophenylhydrazone of acetophenone melted at the same temperature as the known compound.

After distillation of the substance over metallic sodium, it did not give turbidity with a solution of 2,4-dinitrophenylhydrazone:

B.p. 61-62° at 3 mm; d_0^0 0.9371; d_{20}^{20} 0.9257; d_4^{20} 0.9238; n_D^{20} 1.5400, MR_D 43.38. $C_{10}H_8\lceil_4\overline{\overline{\lceil}}$. Calculated 42.31; EMR_D 1.06.

0.0901 g sub.: 0.3092 g CO_2; 0.0521 g H_2O. 0.3122 g sub.: 11.16 g benzene: Δt 1.06°. Found %: C 93.49; H 6.42; M 132. $C_{10}H_8$. Calculated %: C 93.75; H 6.25; M 128.

Ozonization of the substance having a boiling point of 61-62° at 3 mm. 1.8 g of the substance in 35 ml of chloroform was subjected to ozonization. For the ozonization, 1.46 g of ozone (the theoretical quantity was 1.35 g) was used; after absorption of 0.756 g of ozone for 40 minutes, a sharp decrease in the rate of ozonization occurred. The ozonization curve is given in the figure.

Traces of formic acid were observed from the acid which was volatile with water vapor (reacting with mercuric chloride, lead acetate and ammoniacal solution of silver oxide).

After removal of the formic acid with ether, benzoic acid having a m.p. of 119° (after sublimation) was obtained; it did not produce a decrease of the melting point with the known benzoic acid. On continuous digestion in the extractor, oxalic acid having a m.p. of 101° (mixed sample) was obtained. The oxalic acid was converted to the calcium salt.

0.1047 g salt: 0.1122 g $CaSO_4$. Found %: Ca 31.52. C_2O_4Ca. Calculated %: Ca 31.25.

III. Action of 30% Sulfuric Acid on Methylphenylacetylenecarbinol

We heated 2 g of methylphenylacetylenecarbinol with 20 ml of a 30% solution of sulfuric acid under conditions analogous to those used for the action of sulfuric acid on pinacol.

The reaction product was extracted with ether, and the extract was washed with a soda solution, and dried over sodium sulfate. After removal of the ether, the substance was distilled under reduced pressure:

B.p. 98-99° at 3 mm. Literature data for ethylideneacetophenone [29]: b.p. 114-115° at 11 mm.

The substance contained no hydroxyl groups and displayed unsaturated properties.

0.1035 g sub.: 0.3111 g CO_2; 0.0654 g H_2O. Found %: C 81.98; H 7.02. $C_{10}H_{10}O$. Calculated %: C 82.19; H 6.85.

With 2,4-dinitrophenylhydrazine, the substance gave pyrazoline (pyrazoline reaction), having a m.p. of 162° (after two recrystallizations from alcohol).

0.1060 g sub.: 0.2276 g CO_2; 0.0431 g H_2O. 7.21 mg sub.: 1.004 ml N_2 (18°, 772 mm). Found %: C 58.56; H 4.51; N 16.59. $C_{16}H_{14}O_4N_4$. Calculated %: C 58.89; H 4.29; N 17.18.

SUMMARY

1. A new pinacol of the acetylenic series – symmetrical dimethylphenylphenylacetyleneethylene glycol (3-methyl-2,5-diphenylpentyne-4-diol-2,3) was synthesized from methylphenylacetylcarbinol and phenylacetylene by the Iotsich method.

2. On thermal decomposition, pinacol (distillation in vacuo) gave methylphenylcarbinol, diphenyl and a considerable quantity of resins.

3. Pinacol, on the action of 30% sulfuric acid with heating, did not undergo the acetylene-allenic, or the pinacolinic rearrangements, but decomposed into acetophenone and phenylvinylacetylene, wherein initially a dehydration with the formation of an eninic alcohol proceeded, and then cleavage of the acetophenone occurred.

4. It was found that methylphenylacetylenecarbinol isomerizes, on the action of sulfuric acid, to ethylideneacetophenone.

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INVESTIGATIONS OF CONJUGATED SYSTEMS

LV. ORDER OF ADDITION OF THE ALKYLHYPOHALOGENITES TO 3-CHLORO- AND 3-BROMOHEXADIENE-1,3

E. A. Leporskaya and A. A. Petrov

In a preceding communication it was shown that the order of addition of the alkylhypoiodites to the homologs of 2-chlorobutadiene of normal structure, with the alkyl in the primary position of the conjugated system, ($R-CH=CCl-CH=CH_2$), does not differ from their order of addition to the unsaturated 2-chlorobutadiene: the addition proceeds in the 3,4-position [1].

It was of interest to investigate to what extent this rule holds for analogous formation of diene systems with other halogens, and especially with other hypohalogenites, since it was established earlier that the 2-halogenbutadienes add the hypohalogenites differently: the hypoiodites and the hypobromites are added chiefly in the 3,4-position, but the hypochlorites add chiefly in the 1,4-position [2].

For this purpose we investigated the order of addition of the alkylhypobromites and the alkylhypochlorites to 3-chloro- and 3-bromohexadiene-1,3, and also the order of addition of the alkylhypoiodites to the latter substance.

In each case it was possible to expect the formation of 6 isomers:

$R-CH=CCl-CH(OR)-CH_2Hlg$ (I),

$R-CH=CCl-CHHlg-CH_2OR$ (II),

$R-CHHlg-CCl=CH-CH_2OR$ (III),

$R-CH(OR)-CCl=CH-CH_2Hlg$ (IV),

$R-CHHlg-CCl(OR)-CH=CH_2$ (V),

$R-CH(OR)-CClHlg-CH=CH_2$ (VI).

As a result of the action of benzosulfodibromide on a solution of 3-chlorohexadiene in methyl alcohol, a product having a narrow boiling range was obtained, and by the usual method it was demonstrated that it had the 3,4-structure (I). Under the action of alcoholic alkali, the substance split off HBr with the formation of the enol chloroether being studied, which, by shaking with a dilute solution of sulfuric acid, was transformed to an unsaturated chloroketone according to the following scheme:

$$C_2H_5-CH=CCl-CH(OCH_3)-CH_2Br \rightarrow C_2H_5-CH=CCl-C(OCH_3)=CH_2 \rightarrow C_2H_5-CH=CCl-CO-CH_3.$$

Analogous data were obtained also as a result of carrying out a reaction in ethyl alcohol; the 3,4-bromoethers seemed to be practically the only reaction product. The high boiling fractions in both cases did not exceed 10% of the initial substance. They were not closely studied.

Thus, the quantity of the 1,4-products, if they were obtained at all, was considerably smaller here than in the case of 2-chlorobutadiene.

As a result of the action of benzosulfodichloroamide on a solution of 3-chlorohexadiene in methyl alcohol, a product having a fairly narrow boiling range was obtained, and its physical and chemical properties permitted us to record the 3,4-structure for it also.

1) The substance boiled at 74.5-75° (10 mm), i.e., a total of 8° higher than the 1,4-chloroether obtained from 2-chlorobutadiene (b.p. 65-67° at 10 mm), and consequently, might not be the same type as its homologs. (The two CH_2-groups should give a difference in the boiling point of no less than 20°.)

2) Toward alcoholic alkali, a considerable stability was observed. On standing for a period of 6 hours with a 10% alcoholic solution of KOH, the substance lost about 6% of its chlorine. If it is taken into account that the starting material, judging from the analytical data, contained dichlorides, which should react with alkali in the first order, then one might reach the conclusion that under these conditions a very small quantity of the chloroether undergoes decomposition.

The substances having formulas (II-VI) under these conditions should lose all of their chlorine, since they are of an allyl nature (50%). Thus, the product obtained could not contain any considerable quantity of the isomers (II-VI).

On boiling with alcoholic alkali, 40% of the chlorine splits off: thus the enolic chloroether [$C_2H_5-CH=CCl-C(OCH_3)=CH_2$], is formed, in a yield of only 25%, however.

For the most part, the high-boiling fractions obtained, according to the analytical data, undoubtedly contained products of replacement of chlorine by the methoxy group, probably in admixture with unreacted initial substance.

3) On treatment with zinc dust in alcohol solution, about 40% of the substance distilled without change. A light fraction was obtained in very small quantity, which, judging from the boiling point and the data of analysis for the chlorine and the CH_3O-group, consisted by more than 75% of chlorohexadiene, the formation of which was possible from the dichlorides and from all the isomeric chloroethers. This experiment convinced us that the isomers (II, III and V) could not be present in the original substance in any considerable quantity, since upon reaction with zinc dust they should have given diene ethers.

4) As a result of oxidation of the substance by permanganate, a mixture of acids was obtained, the greater part of which consisted of propionic acid, which at least indicated the predominance of the 3,4-isomer in the reaction mixture. Moreover, a small amount of chloroacetic acid was obtained, the source of which also might be the 3,4-isomer. The acid fraction of 100-120° at 10 mm, according to analytical data (for chlorine and OCH_3 to an equal extent) rather closely approached the second possible product of the oxidation of 3,4-chloroether – methoxychloropropionic acid. This fraction contained chlorine and the methoxy group, and besides could not have been a mixture of the oxidation products of the two possible 1,4-products (methoxybutyric and chlorobutyric acids), since in this case each of the acids would have been present in the mixture to an extent exceeding 70%, which, obviously, is impossible. The formation of propionic acid from substances having the formulas (III and V) is impossible.

Thus, the substance obtained must have only the formula (I).

The reaction of benzosulfodichloroamide with a solution of 3-chlorohexadiene in ethyl alcohol, also gives a chloroether having a narrow boiling range and having a structure analogous to the structure of the methyl ether.

The order of addition of the alkylhypohalogenites to 3-bromohexadiene-1,3 is practically no different from that found for 3-chlorohexadiene.

From 3-bromohexadiene, iodine, and mercuric oxide in methyl and ethyl alcohols, 3,4-iodoethers were obtained, and they gave with mild action of alcoholic alkali, the dienic bromoethers, and later, as a result of the hydrolysis of the latter, the unsaturated bromoketone, $C_2H_5-CH=CBr-CO-CH_3$. None of these substances are described in the literature.

In exactly the same way, the action of benzosulfodibromoamide on a solution of 3-bromohexadiene in methyl alcohol gave 3,4-bromoether. The higher fraction was practically absent. As a result of the action of alcoholic alkali on this ether, the same enolic ether was obtained, however with a mixture of products in which the methoxy groups replaced the bromine.

By the action of benzosulfodichloroamide on a solution of 3-bromohexadiene in methyl alcohol, chiefly a 3,4-chloroether was obtained, and it had a boiling point at least 14° higher than that of the isomeric 1,4-chloroether, produced from bromoprene (b.p. 74-76° at 10 mm). Consequently, the substance that we obtained could not be a monotypic homolog of the latter substance. The higher fraction which might consist of 1,4-products consisted of less than 10% of the parent substance.

When the parent substance was treated with an alcoholic solution of an alkali, the bromine atom entered into the reaction to a considerable extent, and the enolic ether was produced in very small quantities, but it was highly contaminated.

As a result of the oxidation and ozonization of the substance, we obtained chiefly propionic acid and a mixture of acids containing the chlorine and methoxy groups. We did not succeed in separating chloroacetic acid or other acids from the mixture.

The constants of the halogen ethers described in the present report are given in the table. The constants of their lower homologs are also given.

TABLE

Substance	Boiling point at 10 mm	d_4^{20}	n_D^{20}	MR_D	
				found	calculated
$CH_2Cl-CH(OCH_3)-CCl=CH_2$ [2]	43-45°	1.1710	1.4612	36.37	36.20
$CH_2Cl-CH(OC_2H_5)-CCl=CH_2$ [2].	51.-52	1.1297	1.4562	40.89	40.82
$CH_2Cl-CH(OCH_3)-CCl=CH-C_2H_5$	74.5-75	1.1133	1.4673	45.65	45.44
$CH_2Cl-CH(OC_2H_5)-CCl=CH-C_2H_5$	83.5-85.5	1.0867	1.4658	50.22	50.05
$CH_2Br-CH(OCH_3)-CCl=CH_2$ [3].	57-58	1.4795	1.4910	39.05	39.11
$CH_2Br-CH(OC_2H_5)-CCl=CH_2$ [3]	63.5-64.5	1.4402	1.4880	42.72	43.72
$CH_2Br-CH(OCH_3)-CCl=CH-C_2H_5$	85-86	1.3257	1.4840	49.11	48.22
$CH_2Br-CH(OC_2H_5)-CCl=CH-C_2H_5$.	94.5-95	1.3097	1.4838	52.75	52.83
$CH_2Cl-CH(OCH_3)-CBr=CH_2$ [3].	58-59	1.4922	1.4920	38.78	39.11
$CH_2Cl-CH(OCH_3)-CBr=CH-C_2H_5$	87.5-88.5	1.3746	1.4930	48.10	48.33
$CH_2Br-CH(OCH_3)-CBr=CH_2$ [3].	68-68.5	1.7613	1.5145	42.07	42.00
$CH_2Br-CH(OCH_3)-CBr=CH-C_2H_5$	97-98.5	1.5917	1.5112	51.21	51.23
$CH_2I-CH(OCH_3)-CBr=CH_2$.	91.5-92	1.9755	1.5531	47.19	47.03
$CH_2I-CH(OC_2H_5)-CBr=CH_2$	97-98	1.8812	1.5435	51.12	51.65
$CH_2I-CH(OCH_3)-CBr=CH-C_2H_5$	115.5-117	1.7845	1.5430	56.84	56.27
$CH_2I-CH(OC_2H_5)-CBr=CH-C_2H_5$	118-120.5	1.7001	1.5340	60.40	60.88

From the table it is possible to draw the following conclusions.

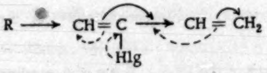
1) An increase of the carbon chain length by two methylene groups produces an increase in the boiling point, at 10 mm, of 28-30° for the chloro- and bromoethers, and of 22-25° for the iodoethers. The specific gravity thus decreased. The index of refraction changed negligibly (in the case of the chloroethers toward an increase, and for the bromo- and iodoethers toward a decrease).

2) Isomeric ethers, differing in the respective positions of their chlorine and bromine atoms, boil at lower temperatures; however, compounds having bromine atoms at the double bond have a considerably larger specific gravity and index of refraction.

3) The molecular refraction found for all the compounds was extremely close to that calculated, which for none of them was found to be extremely elevated. This appeared to confirm the data recorded in the table for substances of the 3,4-series. Some elevation was observed for the halogen ethers of the 1,4-series.

The investigation carried out permits us to draw the following theoretical conclusions:

1. Substitution of a hydrogen atom in the molecule of 2-chlorobutadiene-1,3 or 2-bromobutadiene-1,3 in the alpha-position of the conjugated system is difficult for additions in the 1-position, but is facilitated in the 4-position.



Thus, the effect connected with the presence of the alkyl group (shown by the continuous line), is stronger than that of the specified halogen atom (shown by the dotted line). As a result of this, not only the alkylhypoiodites and alkylhypobromites, but also the alkylhypochlorites, add to the 3-chloro- and 3-bromohexadienes advantageously in the 3,4-position.

It is probable that the alkyl group here also has the well-known steric effect, making the entrance of the part adding to the 1-position of the molecule difficult.

2. For the 2-halogenbutadienes and their homologs, the following law operates: as addition begins with the attack of a halogen atom in the 4-position (homolog of chloro- and bromobutadienes), it proceeds on a series of remaining atoms. On the other hand (chloro- and bromobutadienes), attack in the 1-position completes the formation of the 1,4-product.

Thus, the unusual deviation from the general law in the case of the reaction of the chloro- and bromobutadienes with the alkylhypochlorites (1,4-addition) is connected with the fact that (under conditions of initial attack in the 1-position) the halogen atom in the 2-position prevents attachment of the negatively polarized hydroxy grouping, as a result of which it also enters at the 4-position.

In the case of the hypoiodites and hypobromites, where the reaction begins at the 4-position (as a result of the difficulty of the bromine and iodine atoms entering at the 1-position), the "normal" 3,4-product forms.

EXPERIMENTAL

The 3-chloro- and 3-bromobutadiene-1,3 were produced by a method described previously [1, 4].

I. Action of Benzosulfodibromoamide on a Solution of 3-Chlorohexadiene in Methyl Alcohol

Production of the bromoether. We added 40 g of benzosulfodibromoamide in small portions to a well-mixed solution of 41 g of 3-chlorohexadiene in 120 ml of methyl alcohol at 0-3°. New portions of benzosulfodibromoamide were added after disappearance of the yellow color caused by the previous portions. After standing for a period of 36 hours, the solution contained only traces of active bromine. Later some Na_2SO_3 was added to the solution and it was steam-distilled. When the distillate was diluted with water, an oil separated. The aqueous fraction was fractionally distilled twice; small quantities of oil again being extracted. All the oil portions were combined, washed with a $CaCl_2$ solution, and dried over $CaCl_2$.

By distillation of the substance obtained, under vacuum, the original chlorohexadiene (7 g) was removed. The following fractions (10 mm) were obtained: 1) to 85°, 4.5 g; the second, 85-86°, 29.9 g; the third, 86-90°, 4.4 g; the residue, 1 g.

The yield of the 85-86° fraction at 10 mm amounted to 54% of that calculated on the basis of the bromoamide taken.

The constants for this fraction are presented in the table.

0.1070, 0.1046 g sub.: 0.1517, 0.1490 g AgCl + AgBr. Found %: Cl + Br 49.40, 49.63. $C_7H_{12}OClBr$. Calculated %: Cl + Br 50.70.

Action of alcoholic alkali on the bromoether. To an alcoholic solution of caustic potash (5.5 g of KOH + + 0.1 g of hydroquinone in 20 ml of methyl alcohol), heated on a water bath, small portions of bromomethyl ether (15 g) were added over a period of 15 minutes through a reflux condenser. The mixture was heated for a further 40 minutes, and then was diluted with water and steam-distilled. The oil obtained was washed with water and $CaCl_2$ solution, dried over $CaCl_2$, and distilled under vacuum at 85 mm, whereby we obtained the following fractions: first, 100-102°, 0.6 g; second, 102-103°, 4.6 g; third, 103-105°, 1.1 g; fourth, 105-110°, 0.8 g; fifth, above 110°, 0.8 g.

The yield of the fraction of 100-105° at 85 mm was 65%.

B.p. 102-103° at 85 mm, d_4^{20} 1.0405, n_D^{20} 1.4775.

0.1064 g sub.: 0.1033 g AgCl. Found %: Cl 24.02. $C_7H_{11}OCl$. Calculated %: Cl 24.18.

Found previously for 2-methoxy-3-chlorohexadiene-1,3: b.p. 102-103.5° at 85 mm, d_4^{20} 1.0179, n_D^{20} 1.4792.

Hydrolysis of the enol form of the ether. 6.3 g of 2-methoxy-3-chlorohexadiene-1,3 was shaken at 40-50° with 40 ml of a 5% solution of H_2SO_4 in the presence of hydroquinone (0.05 g) for 2 hours. An oil separated from the aqueous layer and was dried over $CaCl_2$. By distillation under vacuum at 30 mm the following fractions were obtained: first, to 74°, 0.8 g; second, 74.5-76.5°, 3 g; residue, 0.5 g.

The yield of the second fraction amounted to 52% of the calculated:

B.p. 74.5-76.5° (30 mm), d_4^{20} 1.0580, n_D^{20} 1.4703.

0.1130 g sub.: 0.1186 g AgCl. Found %: Cl 25.97. C_6H_9OCl. Calculated %: Cl 26.75.

From the substance a 2,4-dinitrophenylhydrazone having a m.p. of 139° (after recrystallization from a mixture of alcohol and ethyl acetate) was obtained by the usual method.

Found previously for 3-chlorohexen-3-one-2: b.p. 76-77.5° at 30 mm, d_4^{20} 1.0592, n_D^{20} 1.4730. The 2,4-dinitrophenylhydrazone: m.p. 139°.

II. Action of Benzosulfodibromoamide on a Solution of 3-Chlorohexadiene in Ethyl Alcohol

By the usual method, using 15 g of 3-chlorohexadiene, 50 ml of ethyl alcohol and 15 g of benzosulfodibromoamide, we obtained a substance which on distillation gave the initial chlorohexadiene (2.5 g) and then at 10 mm, gave the following fractions: the first at 94°, 1.5 g; second, 94-95°, 13 g; residue, 1.2 g. The yield of bromoether was 43%. The second fraction, after repeated distillation, gave a product chiefly at 94-94.25° (10 mm). Its constants are given in the table.

0.1208, 0.1130 g sub.: 0.1690, 0.1576 g AgCl + AgBr. Found %: Cl + Br 48.74, 48.60. $C_8H_{14}OClBr$. Calculated %: Cl + Br 47.76.

III. Action of Benzosulfodichloroamide on a Solution of 3-Chlorohexadiene in Methyl Alcohol

Production of chloroether. From 44 g of benzosulfodichloroamine, 65 g of 3-chlorohexadiene in 200 ml of methyl alcohol under the conditions described in Section I, we obtained a substance which on distillation gave the following fractions (10 mm): first, to 60°, 9.8 g (chlorohexadiene); second, 60-70°, 0.7 g; third, 70-74.5°, 1.5 g; fourth 74.5-75°, 34.3 g; fifth, 75-80°, 6 g; residue, 1.2 g. The yield of the third, fourth and fifth fractions having a b.p. 70-80° (10 mm) was 59% (based on dichloroamide).

For the fourth fraction: b.p. 74.5-75° at 10 mm, d_4^{20} 1.1175, n_D^{20} 1.4682.

0.1079 g sub.: 0.1735 g AgCl. Found %: Cl 39.75. $C_7H_{12}OCl_2$. Calculated %: Cl 38.77.

In order to purify the dichlorides, 59 g of chloroether was carefully mixed with a solution of 3.3 g of KOH in 30 ml of methyl alcohol (0.2 mole KOH per mole of ether). The mixture was allowed to stand at 0° for 3-4 hours and at room temperature for about 2 hours, and was then diluted with water.

The purified ether, on distillation under vacuum at 10 mm, gave the following fractions: first, to 72.5°, 4 g; second, 72.5°, 3.8 g; third 73.5-76°, 46 g. The yield (second and third fractions) was 85%. The constants of the main fractions are given in the table.

0.1164 g sub.: 0.1839 g AgCl. Found %: Cl 39.08. $C_7H_{12}OCl_2$. Calculated %: Cl 38.77.

In the water layer, 0.36 g of chloride ion was found, which amounts to 6% of that present in the substance.

Action of an alcoholic solution of KOH on the chloroether. From 30 g of the chloroether, freed from dichlorides, the action of a solution of 14 g of KOH in methyl alcohol produced 21 g of an oil. The aqueous part in this case was extracted several times with ether. In it 4.89 g of chloride ion was found, and this amounted to 41% of the total chlorine in the original chloroether.

The following fractions were obtained by distillation of the oil: first, to 100°, 0.5 g; second, 101-105°, 5.5 g; third, 105-120°, 1.2 g; fourth, 120-127°, 12.5 g.

Repeated distillation of the second fraction gave the dienic chloroether:

B.p. 102-103.5° (85 mm), d_4^{20} 1.0134, n_D^{20} 1.4767. MR_D 40.85. $C_7H_{11}OCl$. Calculated 40.10.

0.1052 g sub.: 0.1020 g AgCl. Found %: Cl 23.96. $C_7H_{11}OCl$. Calculated %: Cl 24.13.

From the dienic chloroether, by the usual method, we obtained the unsaturated chloroketone:

B.p. 75-76.5° (30 mm), d_4^{20} 1.0507, n_D^{20} 1.6725. The 2,4-dinitrophenylhydrazone: m.p. 138.5°.

We obtained 10 g of a substance by distillation of the fourth fraction:

B.p. 87-92° (20 mm), d_4^{20} 1.0424, n_D^{20} 1.4540.

0.1201 g sub.: 0.1331 g AgCl. 0.2502 g sub.: 0.4536 g AgI (according to Zeisel). Found %: Cl 27.42; OCH_3 23.96. $C_7H_{12}OCl_2$. Calculated %: Cl 38.77; OCH_3 16.95. $C_8H_{15}O_2Cl$. Calculated %: Cl 19.85; OCH_3 34.74.

Action of zinc dust on a water-alcohol solution of the chloroether. Into a flask fitted with a dropping funnel and a fractionating column, 40 g of zinc dust, 70 ml of ethyl alcohol, and 30 ml of water were placed. The mixture was brought to boiling, after which, through the dropping funnel, 25 g of chloroether was added in small portions. The reaction products were distilled, first with alcohol and water, then with water. From the oil obtained by distillation, 2 g of substance was separated:

B.p. 122-127°, d_4^{20} 0.9027, n_D^{20} 1.4630.

0.1158 g sub.: 0.1075 g AgCl. 0.1250 g sub.: 0.0672 g AgI (according to Zeisel). Found %: Cl 22.94; OCH_3 7.10.

Moreover about 10 g of the following substance was obtained:

B.p. 88-90° (200 mm), d_4^{20} 1.1053, n_D^{20} 1.4650.

0.1206 g sub.: 0.1865 g AgCl. Found %: Cl 38.25. $C_7H_{12}OCl$. Calculated %: Cl 38.77.

By treatment with an alcoholic solution of alkali we obtained 0.7 g of the corresponding enolic ether:

B.p. 100-105° (85 mm), d_4^{20} 1.0283, n_D^{20} 1.4760.

Oxidation of the chloroether with potassium permanganate. To a mixture of 15.3 g of chloromethyl ether and a solution of 26.5 g of $MgSO_4$ in 120 ml of water, we added dry potassium permanganate in small portions, with stirring (depending on the extent of decolorization). After completion of the reaction, the manganese dioxide was filtered off, and washed with small quantities of water. From the filtrate, acidified with 40% H_2SO_4, the acids were extracted by ether in an extractor. On distillation of the acids the following substances were obtained.

a) Propionic acid (about 2.5 g). The main part of the fraction boiled at 139-141°. From the acids (by the action of thionyl chloride, and then aniline in ether solution) we obtained the anilide having a m.p. of 104°, which corresponds to the literature data [5].

b) A mixture of acids having a b.p. of 180-205° (1.8 g), from which 0.6 g of chloroacetic acid having a m.p. of 61.5-62.5° was separated [5].

0.0894 g sub.: 0.1369 g AgCl. Found %: Cl 37.71. $C_2H_3O_2Cl$. Calculated %: Cl 37.52.

The residue, after separation of the chloroacetic acid, gave the following results for the analysis for chlorine and methoxy groups:

0.1241 g sub.: 0.1380 g AgCl. 0.1026 g sub.: 0.0692 g AgI (according to Zeisel). Found %: Cl 27.51; OCH_3 8.91.

c) A mixture of acids (1.5 g) having a b.p. of 100-120° at 10 mm.

0.1075 g sub.: 0.0923 g AgCl. 0.1405 g sub.: 0.2049 g AgI (according to Zeisel). Found %: Cl 21.45; OCH_3 19.27.

IV. Action of Benzosulfodichloroamide on a Solution of 3-Chlorohexadiene in Ethyl Alcohol

From 17.5 g of ethylchloroprene, 100 ml of ethyl alcohol and 14 g of benzosulfodichloroamide, an oil was produced, and on distillation under vacuum of 10 mm it gave the following fractions: first, to 83.5°, 1.5 g; second, 83.5-85.5°, 7.5 g; third, 85.5-87°, 1.4 g; residue, 0.5 g.

The yield of the second and third fractions was 38% (based on the amount of benzosulfodichloroamide taken).

B.p. 83.5-87° (10 mm), d_4^{20} 1.0992, n_D^{20} 1.4670.

0.1090 g sub.: 0.1678 g AgCl. Found %: Cl 38.08. $C_8H_{14}OCl$. Calculated %: Cl 36.82.

Since the substance contained an excess of chlorine in comparison to the theoretical amount, it was subjected to purification (see Section III) by treatment in the cold with an alcoholic solution of KOH (7 g of chloroether, 0.36 g of KOH + 4 ml of alcohol).

By distillation of the purified product the following fractions were obtained: first, to 83°, 1.1 g; second, 83.5-85.5°, 4.5 g; residue, 0.6 g.

The yield of the 83.5-85.5° fraction was 73%. The constants are given in the table.

0.0440 g sub.: 0.0667 g AgCl. Found %: Cl 36.94. $C_8H_{14}OCl_2$. Calculated %: Cl 36.82.

The aqueous solution contained 0.16 g of chloride ion, i.e., 6.2% of that present in the original substance.

V. Action of Iodine and Mercuric Oxide on a Solution of 3-Bromohexadiene in Methyl Alcohol

By the usual method, 28 g of iodoether was obtained from 24 g of 3-bromohexadiene, 38 g of iodine and 21 g of mercuric oxide in 50 ml of methyl alcohol.

As a result of distillation of the substance under vacuum, the following fractions were separated: first, to 115.5°; 3.8 g; second, 115.5-117°, 19.0 g; third 117-119°, 2.8 g; residue, 0.8 g.

The constants of the main fraction are given in the table.

0.1296, 0.1254 g sub.: 0.1726, 0.1668 g AgBr + AgI. 0.1022 g sub.: 0.0832 g AgI (according to Zeisel). Found %: Br + I 65.18, 65.10; OCH_3 10.76. $C_7H_{12}OBrI$. Calculated %: Br + I 64.84; OCH_3 9.73.

Action of alcoholic alkali on the iodoether. We obtained 11.5 g of an oil from 25 g of iodoether and 5 g of KOH (10% excess) in 55 ml of methyl alcohol (the alkaline solution was added to the iodoether with stirring). Distillation at 20 mm gave the fractions: first, 80-83°, 2 g; second, 83-84.5°, 4.6 g; third, 84.5-88.5°, 1.7 g; residue, 3.8 g. At the time of distillation we observed the polymerization of the substance.

For the main (second) fraction the following were found:

d_4^{20} 1.2930, n_D^{20} 1.5040. MR_D 43.76. $C_7H_{11}OBr$. Calculated 43.00.

0.1026 g sub.: 0.1003 g AgBr. Found %: Br 41.60. $C_7H_{11}OBr$. Calculated %: Br 41.83.

Production of the ketone. From 4.5 g of the enolic form of the bromoether we obtained 3 g of bromoketone by the usual method. A major part of the substance boiled at 70.5-71° (10 mm);

d_4^{20} 1.3784, n_D^{20} 1.5010. MR_D 37.83. C_6H_9OBr. Calculated 37.22.

0.1126 g sub.: 0.1184 g AgBr. Found %: Br 44.75. C_6H_9OBr. Calculated %: Br 45.14.

The 2,4-dinitrophenylhydrazone of the ketone after recrystallization from ethyl acetate had a m.p. of 140-141°.

4.3 mg sub.: 0.512 ml N_2 (22°, 762 mm). Found %: N 15.43. $C_{12}H_{13}O_4N_4Br$. Calculated %: N 15.73.

VI. Action of Benzosulfodibromoamide on a Solution of 3-Bromohexadiene in Methyl Alcohol

From 16 g of 3-bromohexadiene, 12.7 g of benzosulfodibromoamide and 50 ml of methyl alcohol at 5-7°, we produced 16.5 g of a substance, which on distillation under vacuum at 10 mm gave the following fractions: first, to 94.0°, 3 g (original bromohexadiene), second, 94-97°, 2.1 g; third, 97-98.5°, 10.0 g; fourth, 98.5-100°, 1.5 g; residue, 1.5 g. The constants of the main fraction are given in the table.

0.1436, 0.1202 sub.: 0.1989, 0.1656 g AgBr. Found %: Br 58.94, 58.63. $C_7H_{12}OBr_2$. Calculated %: Br 58.76.

On heating 15 g of bromoether with 4 g KOH in 20 ml of methyl alcohol we obtained 7 g of a substance, giving the following fractions on distillation (20 mm): first, 73-81°, 1.0 g; second, 81-84°, 3.3 g; residue, 2 g. For the main (second) fraction we found:

d_4^{20} 1.2477, n_D^{20} 1.4950.

0.1321 g sub.: 0.1196 g AgBr. Found %: Br 39.43. $C_7H_{11}OBr$. Calculated %: Br 41.83.

The hydrolysis of 3.2 g of the substance with 5% H_2SO_4 gave 1.1 g of ketone:

B.p. 70-71.5° (10 mm), d_4^{20} 1.3213, n_D^{20} 1.4925.

0.1193 g sub.: 0.1164 g AgBr. Found %: Br 41.52. C_6H_9OBr. Calculated %: Br 45.14.

VII. Action of Benzosulfodichloroamide on a Solution of 3-Bromohexadiene in Methyl Alcohol

From 32 g of 3-bromohexadiene, 19 g of benzosulfodichloroamide and 100 ml of methyl alcohol at 5-10°, we obtained 23 g of an oil. Distillation at 10 mm gave the following fractions: first, to 80°, 2.7 g; second, 80-87.5°, 1.6 g; third, 87.5-88.5°, 13.8 g; fourth, 88.5-92°, 1 g; residue, 1.5 g.

The constants of the main fraction are given in the table.

0.1400 g sub.: 0.2086 g AgCl + AgBr. Found %: Cl + Br 50.67. $C_7H_{12}OClBr$. Calculated %: Cl + Br 50.70.

By the action of 3.8 g of KOH in 45 ml of methyl alcohol on 10 g of the substance, we obtained an oil, giving on distillation (20 mm) the following fractions: first, 77-80°, 1.7 g; second, 80-101°, 1.0 g; third, 101-102°, 2.8 g; residue, 0.5 g. For the first fraction we found the following:

B.p. 77-80° (20 mm), d_4^{20} 1.0120, n_D^{20} 1.4550.

0.1050 g sub.: 0.0483 g AgBr. 0.2062 g sub.: 0.4894 g AgI (according to Zeisel). Found %: Br 19.58; OCH_3 31.37. $C_6H_{11}OBr$.* Calculated %: Br 41.80; OCH_3 16.24.

For the third fraction we found:

B.p. 101-102° (20 mm), d_4^{20} 1.3017, n_D^{20} 1.4810.

0.1074 g sub.: 0.1364 g AgCl + AgBr. 0.1586 g sub.: 0.2274 g AgI (according to Zeisel). Found %: Cl + Br 45.22; OCH_3 18.44. $C_7H_{12}OClBr$.** Calculated %: Cl + Br 50.70; OCH_3 15.67.

As a result of the ozonization of 6.5 g of the substance in chloroform (the ozonide decomposed 5% H_2O_2) we obtained two main acid fractions. One of them (1.3 g) was propionic acid. Its anilide had a m.p. of 104°. The second was a fraction having a wide boiling interval and represented a mixture of acids, containing OCH_3 or Cl, possibly partially decomposed during the process of ozonization. For the second fraction, the b.p. was 200-220° (2.2 g).

0.1250 g sub.: 0.1904 g AgCl. 0.1060, 0.0822 g sub.: 0.1251, 0.0966 g AgI (according to Zeisel). Found %: Cl 21.65; OCH_3 15.60, 15.53. $C_4H_7O_3Cl$. Calculated %: Cl 25.59; OCH_3 22.39. $C_4H_7O_2Cl$. Calculated %: Cl 28.95. $C_5H_{10}O_3$. Calculated %: CH_3O 26.30.

The residue in the flask, according to the analytical data, almost approached methoxychloropropionic acid.

0.0850 g sub.: 0.0858 g AgCl. 0.0612 g sub.: 0.0912 g AgI (according to Zeisel). Found %: Cl 23.95; OCH_3 19.83. $C_4H_7O_3Cl$. Calculated %: Cl 25.59; OCH_3 22.39.

SUMMARY

1. The order of addition of the alkylhypohalogenites to 3-chloro- and 3-bromohexadiene-1,3 was investigated.

2. It was shown that in all cases, chiefly the ethers of 1,3-halogenhexen—3-ol-2 were obtained.

3. Differences in the order of addition of the alkylhypohalogenites to the halogenhexadienes, in comparison with the halogenbutadienes, were accounted for on the basis of the theory of electronic displacement.

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[2] A. A. Petrov, J. Gen. Chem., 22, 1516 (1952).****

[3] A. A. Petrov, J. Gen. Chem., Supplement I, 362 (1953).

[4] E. A. Leporskaya and A. A. Petrov, J. Gen. Chem., 23, 1471 (1953).*****

[5] Dictionary of Organic Compounds. Foreign Lit. Press, Vol. I, 421 (1949); Vol. III 518 (1949).

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* Calculation made starting from the assumption that the compound contains only bromine.

** It was assumed that the substance was contaminated with chloroether.

*** See Consultants Bureau Translation, page 1091.

**** See Consultants Bureau Translation, page 1557.

***** See Consultants Bureau Translation, page 1537.

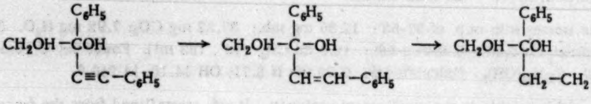
SYNTHESIS AND TRANSFORMATION OF α-GLYCOLS OF THE ETHYLENE SERIES

III. PRODUCTION OF 2,4-DIPHENYLBUTEN-3-DIOL-1,2

L. F. Chelpanova and N. M. Libman

Earlier one of us, together with Z. V. Printseva [1], described the production of 2-methyl-3,5-diphenylpenten 4-diol-2,3, by reduction of the corresponding α-glycols of the acetylene series, in the presence of colloidal palladium. We also used this method for obtaining 2,4-diphenylbutene-3-diol-1,2 (II).

The acetylene glycol necessary for this reaction – the asymmetrical phenylphenylacetyleneethyleneglycol (m.p. 101-102°) (2,4-diphenylbutyne-3-diol-1,2) (I) which has not been described in the literature, was synthesized according to the Iotsich method, starting from benzoylcarbinol and phenylacetylene.



(I) (II) (III)

During the reduction of the α-glycols of the acetylene series (I), in the presence of colloidal palladium, two geometrical isomers of the corresponding ethyleneglycol (II), with m.p. of 52-53° and 68-70°, were isolated.

Both isomers, on further hydrogenation in the presence of platinum black, gave the same saturated glycol having a m.p. of 57-58° (III). This saturated glycol was obtained by reduction of 2,4-diphenylbutyne-3-diol-1,2 (I) in the presence of platinum black.

EXPERIMENTAL

2,4-Diphenylbutyne-3-diol-1,2

To phenylacetylene magnesium bromide, prepared in the usual way from 6 g of magnesium and 25 g of ethyl bromide and 25 g of phenylacetylene, 10 g of benzoylcarbinol dissolved in 250 ml of anhydrous ether was added. The reaction was started at 20° and continued at room temperature for a period of 3 hours. On the following day, the complex was decomposed by ice water, and later by 5% solution of sulfuric acid at 0°. The product was extracted with ether, and the ether extract was washed with a 5% solution of soda, and dried over Na_2SO_4.

After removal of the ether, the solid substance was filtered off and washed on the filter three times with benzene. After recrystallization from a mixture of sulfuric acid and petroleum ether (1:1), needle-shaped white crystals having a m.p. of 101-102° were obtained. The yield was 15 g (86%). The substance dissolved well in alcohol, benzene, ether, ethyl acetate, acetone, dioxan, and difficultly in ligroin and petroleum ether.

With concentrated H_2SO_4 the substance gave a dark red color, and it decolorized a solution of potassium permanganate and a solution of bromine in chloroform. On heating with potash, according to the method of Babayan [2], the substance decomposed, yielding phenylacetylene, which was observed with an ammoniacal solution of silver oxide.

7.15 mg sub.: 21.09 mg CO_2; 3.60 mg H_2O. 0.1658 g sub.: 19.52 g benzene Δt 0.18°. 0.0212 g sub.: 4.2 ml CH_4 (15°, 765 mm). Found %: C 80.59; H 5.63; OH 14.09; M 239. $C_{16}H_{12}(OH)_2$. Calculated %: C 80.65; H 5.92; OH 14.28; M 238.

2,4-Diphenylbutene-3-diol-1,2

Reduction of the α-glycols of the acetylene series was carried out in the usual way by the method of catalytic hydrogenation in the presence of colloidal palladium [1].

2.38 g of acetylene glycol, dissolved in 50 ml of ethyl alcohol, in the presence of 5 mg of colloidal palladium, absorbed 248 ml of hydrogen (25°, 770 mm) in 8 minutes, instead of 247.5 ml, the amount theoretically required for conversion of the triple bond to a double bond.

After separation of the catalyst and removal of the solvent, a substance contaminated by an oily mixture was obtained. The substance was washed with cold petroleum ether and repeatedly recrystallized from petroleum ether (boiling point at 60°): after several recrystallizations from petroleum ether, a substance having a m.p. of 52-53° was separated from the first fraction, and from the latter – a substance, more soluble in petroleum ether and having a m.p. of 68-70°, was obtained. Both products gave a violet opalescence with concentrated H_2SO_4, and both decolorized bromine in chloroform and potassium permanganate solution.

Hydrogenation of both substances in the presence of platinum black gave the same saturated glycol having a m.p. of 56-57°.

1.19 g of ethylene glycol having a m.p. of 52-53°, dissolved in 30 ml of ethyl alcohol, in the presence of 0.25 g of platinum black, during 18 minutes absorbed 53 ml of hydrogen (17°, 752 mm), the theoretical amount required for converting the double bond to a single bond. A similar quantity of ethylene glycol having a m.p. of 68-70°, under similar conditions, absorbed the same quantity of hydrogen.

On the basis of these data it was possible to assume that the substances having m.p. of 52-53° and 68-70° were geometrical isomers and that, apparently, the substance having the m.p. of 52-53° corresponds to the cis-isomer, and that having a m.p. of 68-70° – the trans-isomer.

Investigation of the isomer with m.p. of 52-53°: 12.80 mg sub.: 37.32 mg CO_2; 7.92 mg H_2O. 0.1649 g sub.: 12.55 g benzene: Δt 0.28°. 0.0647 g sub.: 12.8 ml CH_4 (18°, 753 ml). Found %: C 79.57; H 6.92; OH 13.61; M 238.0. $C_{16}H_{14}(OH)_2$. Calculated %: C 79.98; H 6.71; OH 14.16; M 240.0.

The substance was highly soluble in the usual organic solvents. It was crystallized from the fraction of petroleum ether having a b.p. of 65°.

Investigation of the isomer with m.p. of 68-70°: 12.60 mg sub.: 37.11 mg CO_2; 7.73 mg H_2O. 0.1278 g sub.: 14.8 g benzene: Δt 0.18°. 0.028 g sub.: 6.0 ml CH_4 (24°, 756 mm). Found %: C 80.38; H 6.86; OH 14.45; M 243. $C_{16}H_{14}(OH)_2$. Calculated %: C 79.98; H 6.71; OH 14.16; M 240.0.

The substance having a m.p. of 68-70° dissolved better in petroleum ether than did the substance having a m.p. of 52-53°.

2,4-Diphenylbutanediol-1,2

A saturated glycol was obtained by hydrogenation of acetylene glycol in the presence of colloidal palladium: 2.38 g of acetylene glycol, dissolved in 50 ml of ethyl alcohol, in the presence of 5 mg of colloidal palladium, during 19 minutes absorbed 495 ml of hydrogen (25°, 770 mm), the theoretical amount required for conversion of the triple bond to a single bond.

Furthermore, the saturated glycol was obtained also in the presence of platinum black: 1.19 g of acetylene glycol, dissolved in 25 ml of ethyl alcohol, in the presence of 0.3 g of platinum black absorbed 107 ml of hydrogen (17°, 752 mm) for 35 minutes. After addition of 4 atoms of hydrogen, the reaction was stopped. The catalyst was filtered off and the solvent was removed. A syrup, which did not crystallize, was obtained. After partial removal of the ether, colorless needle-shaped crystals having a m.p. of 56-57° were deposited.

The substance was highly soluble in alcohol, ether and benzene, and poorly soluble in gasoline and petroleum ether. It did not give a violet opalescence with concentrated H_2SO_4.

11.31 mg sub.: 32.98 mg CO_2; 7.57 mg H_2O. 0.1010 g sub.: 12.25 g benzene: Δt 0.17°. 0.0250 g sub.: 50 ml CH_4 (24°, 756 mm). Found %: C 79.58; H 7.49; OH 13.48; M 246. $C_{16}H_{16}(OH)_2$. Calculated %: C 79.31; H 7.49; OH 14.04; M 242.0.

Oxidation of saturated glycol by manganese triacetate [3]. Into a flask were placed 3 g of saturated glycol and 5 g of manganese triacetate, dissolved in 100 ml of glacial acetic acid. After 3 hours of heating on the water bath at 60-70°, the solution acquired a yellow color. On the following day, the manganese diacetate was filtered off, and the filtrate was neutralized and steam-distilled. A crystalline substance, which after recrystallization from alcohol had a m.p. of 69-70°, was obtained. With 2,4-dinitrophenylhydrazine, the substance gave the 2,4-dinitrophenylhydrazone having a m.p. of 143-145°. The melting point of this substance corresponds to that of the ketone – $C_6H_5CH_2-CH_2-CO-C_6H_5$ – phenylpropiophenone [4].

Since phenylpropiophenone was obtained from the oxidation of the saturated glycol by manganese triacetate, this demonstrated the structure not only of the saturated, but also of both the ethylenic and acetylenic glycols.

SUMMARY

1. A new glycol of the acetylenic series, 2,4-diphenylbutyne-3-diol-1,2, having a m.p. of 101-102° was synthesized.

2. Two geometrical isomers of ethylene glycol – 2,4-diphenylbutene-3-diol-1,2 – having a m.p. of 52-53° and 68-70°, and not described in the literature, were obtained.

3. Both glycols of the acetylenic and ethylenic series yielded, by catalytic reduction, the same saturated glycol – 2,4-diphenylbutanediol-1,2 having a m.p. of 56-57°.

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[2] A. T. Babayan, J. Gen. Chem., 9, 396 (1939).

[3] S. Zonis and Yu. Kornilova, J. Gen. Chem., 20, 1252 (1950).**

[4] Beilst, VII, 444.

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Lensoviet Leningrad Institute of Technology

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* See Consultants Bureau Translation, page 1189.

** See Consultants Bureau Translation, page 1306.

[illegible]

(1) [illegible]

(2) A. T. Babayan, J. Gen. Chem. [illegible]

(3) [illegible]

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* See Consultants Bureau Translation, page [illegible].

** See Consultants Bureau Translation, page [illegible].

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INVESTIGATION OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

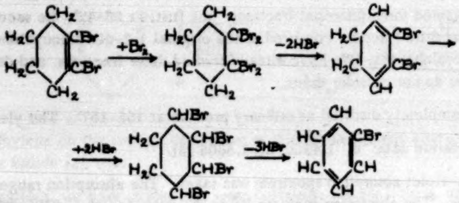
XIV. FORMATION OF BROMOBENZENE BY REACTION OF MOLECULAR BROMINE WITH 1,2-DIBROMOCYCLOHEXENE-1

N. A. Domnin and A. S. Beletskaya

One of us [1] has shown that, by reacting molecular bromine with 1,2-dibromocyclohexene-1 under relatively mild conditions, a mixture of products, consisting of 1,1,2,2-tetrabromocyclohexene, o-dibromobenzene and bromobenzene is formed. Then a simple and fundamental explanation for the formation of 1,1,2,2-tetrabromocyclohexane and o-dibromobeznene was given. The problem of the formation of bromobenzene remained unclarified, and moreover, we showed its presence in the mixture of reaction products only by the method of nitration, which, as we showed later, appared to be unsuitable. Together with this, however, the problem of the mechanism of the formation of bromobenzene in the indicated reaction is of considerable interest, and because of this, we again return to the investigation of this problem.

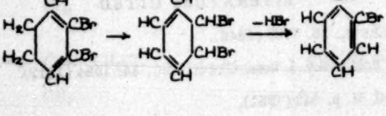
As a result of the present work, we found that the formation of bromobenzene by the reaction of molecular bromine and 1,2-dibromocyclohexene-1 was a fact. The certainty of the presence of bromobenzene in the mixture was demonstrated by ultra-violet absorption spectroscopy.

Regarding the mechanism of formation of bromobenzene, as a result of a critical consideration of different possibilities, we represent it in the following form:



Of all the substances indicated in this scheme, the only intermediate substance which was not isolated appears to be 1,2,3,4-tetrabromocyclohexane; we isolated and characterized earlier the four remaining substances.

It is well-known that a halogen derivative of a type such as tetrabromocyclohexane is very easily transformed to an aromatic nucleus. Moreover, for the formation of bromobenzene, we present still another reasonable possibility, which may be expressed by the following scheme:



As seen from the scheme given, we assume that 2,3-dibromocyclohexadiene-1,3 undergoes preliminary isomeric transformation to 2,3-dibromocyclohexadiene-4,6, which, giving up a molecule of hydrogen bromide, is transformed to bromobenzene.

EXPERIMENTAL

By reaction of phosphorus pentachloride with cyclohexane, a mixture consisting of 1-chlorocyclohexene-1 and 1,1-dichlorocyclohexane was obtained. The splitting off of hydrogen chloride was accomplished by the use of quinoline, dimethylaniline and a 20% alcoholic solution of caustic potash.

Cleavage by quinoline. Into a flask with a cover, 71 g of freshly distilled quinoline was placed, and heated to boiling. Into the boiling quinoline, 55 g of the mixture of chlorides was introduced dropwise from a separatory funnel. The quinoline was used in an amount that was 1.5 times larger than the theoretically required quantity. The monochloride which formed was removed, and in proportion to its removal, a mixture of chlorides was introduced dropwise. After addition of the total mixture of chlorides, the reaction mixture was heated to the point where the temperature of removal did not rise above 144-150°. The monochloride obtained was washed with dilute (1:1) sulfuric acid in order to partially combine the quinoline coming off with the monochloride, then it was washed with water and dried over calcium chloride. The monochloride was distilled several times. We obtained 30 g of a substance having a b.p. of 140-145° (d_4^{15} 1.0403; n_α^{19} 1.4767). The yield was 70%.

The monochloride formed by cleavage brought about by dimethylaniline was more difficult to remove from the mixture, and the cleavage brought about by alcoholic alkali involved formation of an emulsion that we did not succeed in breaking; therefore, we recommend that the liberation of hydrogen chloride be carried out by means of quinoline.

The synthesis of 1-chloro -1,2-dibromocyclohexane was carried out by a method already described [2]. After a double recrystallization from alcohol, a product having a m.p. of 43-44° was obtained, and it was treated with 20% alcoholic solution of caustic potash (30% excess). As a result, 1,2-dibromocyclohexene-1 was obtained, and it melted at 39-40° after a double recrystallization from alcohol.

Bromination of 1,2-dibromocyclohexene-1. To 20 g of 1,2-dibromocyclohexene-1 in a solution of chloroform (1:1), 42 ml (13.4 g) of bromine in chloroform (1:1) was added, with chilling. After addition of all the bromine, the reaction mixture stood for a day at room temperature, and then was heated on a water bath for a period of 2 hours at a temperature of 30-40°, during which hydrogen bromide was liberated. Decolorization of the solution did not take place, therefore, the unreacted bromine was combined with a sodium sulfite solution. The solution was washed with water, dried over calcium chloride, and the chloroform removed in vacuo. The residue was distilled in vacuo at 3 mm. We obtained three principal fractions: the first, at 36-42°, the second, at 74-90°, and the third, at 90-100°. The second and third fractions consisted of the original 1,2-dibromocyclohexene-1, o-dibromobenzene and 1,1,2,2-tetrabromocyclohexane. We have already studied these fractions, and described their products; therefore, in the present report we do not consider them.

The first fraction almost completely distilled at ordinary pressure at 155-157°. The yield was 8%.

d_4^{20} 1.4980; n_D^{20} 1.5600; literature data: d_4^{17} 1.4950; n_D^{20} 1.5605 [3].

For this substance, an ultra-violet absorption spectrum was taken. The absorption range coincided with the absorption range of bromobenzene. The absorption maxima lie at the wave lengths: 2720, 2700, 2650 and 2560 A.

SUMMARY

1. It was shown that by reaction of molecular bromine with 1,2-dibromocyclohexene, besides 1,1,2,2-tetrabromocyclohexane and o-dibromobenzene, up to 8-10% of bromobenzene also formed, and its presence in the mixture was demonstrated spectroscopically.

2. Two possible schemes for the formation of bromobenzene were suggested.

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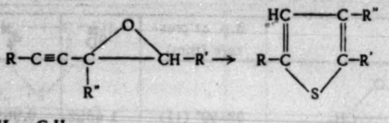
REACTION OF THE α-OXIDES OF THE ACETYLENE SERIES WITH HYDROGEN SULFIDE. III

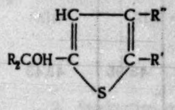
F. Ya. Perveev and N. I. Kudryashov

It was found earlier that, by reacting oxides of the acetylene and vinylacetylene series with hydrogen sulfide in the presence of barium hydroxide, the formation of the corresponding homologs of thiophene takes place [1]:



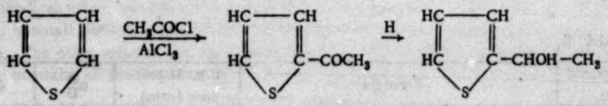
where R = CH_3-, $CH_2{=}CH-$, C_6H_5-;
R' = H, CH_3- and R" = CH_3-, C_2H_5-.

In the present work we decided to use the method described earlier for obtaining hydroxyalkylthiophenes of the type (A).



(A)

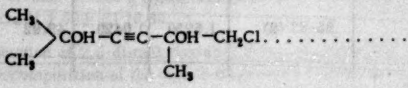
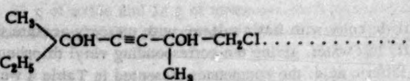
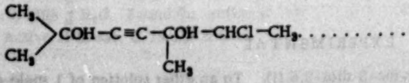
A similar synthesis, except for the theoretical values, may be used in laboratory practice, since until this time a single-stage synthesis of hydroxyalkylthiophene had not been described. Similar compounds were obtained by acylation of thiophene and its homologs [2] by the Friedel-Crafts method, and subsequent reduction of the acylthiophenes [3, 6]



or by the action of ethylene on the sodium derivative of thiophene [4], and also by the action of formaldehyde on thiophene magnesium iodide [5], etc..

For the investigations, we took oxides that were colorless, viscous liquids, and were highly soluble in water, alcohol and ether (Table 2).

TABLE 1

Compound No.	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	MR_D	
					found	calc'd.
(I)	 $(CH_3)_2COH{-}C{\equiv}C{-}\underset{CH_3}{\underset{\vert}{C}}OH{-}CH_2Cl$	115-116° (5)	1.4840	1.1284	44.79	45.06
(II)	 $(CH_3)(C_2H_5)COH{-}C{\equiv}C{-}\underset{CH_3}{\underset{\vert}{C}}OH{-}CH_2Cl$	105-106 (2)	1.4868	1.1121	49.35	49.67
(III)	 $(CH_3)_2COH{-}C{\equiv}C{-}\underset{CH_3}{\underset{\vert}{C}}OH{-}CHCl{-}CH_3$	105-106 (2)	Decomposition		–	–

The synthesis of the acetylenic γ-oxyalcohols was carried out by starting from the chloroglycols of the acetylenic series (Table 1), which in turn were synthesized by the Iotsich method: to ethyl magnesium bromide, with intense stirring and without chilling, the calculated quantity of acetylenecarbinol was added. After addition of the chloroketone, the reaction mixture was treated in the usual way after 12-14 hours.

The reaction of the γ-oxyalcohols with hydrogen sulfide proceeds smoothly. The method of production included the following: into 150 ml of water and 20 g of $Ba(OH)_2$ placed in a round-bottomed flask, hydrogen sulfide was passed for a period of several minutes with intense stirring; then, slowly, the oxide was added dropwise (not discontinuing the supply of hydrogen sulfide). The rate of addition was regulated so that the temperature of the reaction mixture did not exceed 50-60°. After the oxide was run in, hydrogen sulfide was again passed through for a period of 1 hour. After treatment of the reaction mixture, the corresponding hydroxythiophene was isolated. The constants of the compounds obtained are presented in Table 3.

TABLE 2

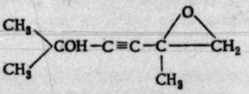
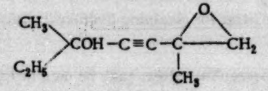
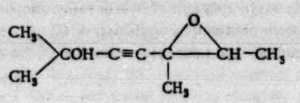
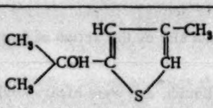
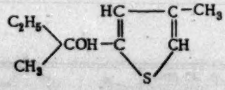
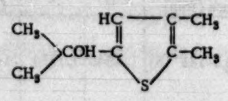
Compound No.	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	MR_D found	calculated
(IV)		98-99° (11)	1.4622	0.9890	38.95	38.81
(V)		81-82 (2)	1.4650	0.9747	43.73	43.43
(VI)		80-81 (3)	1.4618	0.9637	43.95	43.43

TABLE 3

Compound No.	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	MR_D found	calculated
(VII)		100-101° (9) m.p. 47-48°	—	—	—	—
(VIII)		88-89 (3)	1.5240	1.0492	50.2	50.07
(IX)		85-87 (2)	1.5230	1.0420	49.92	50.07

The compounds obtained gave a characteristic color with isatin sulfate; with mercury acetate they formed mercury derivatives; during storage they gradually lost water, giving the corresponding vinyl thiophenes. On treatment of the hydroxyalkylthiophenes with dilute sulfuric acid, the compounds presented in Table 4 were precipitated.

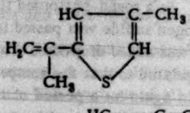
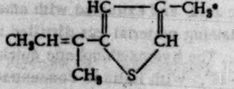
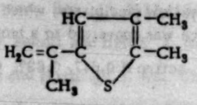
EXPERIMENTAL

1. Production of chloro-2,5-dimethyl-hexine-3-diol-2,5 (I). To an ether solution of 1 mole of ethyl magnesium bromide, with intense stirring and at room temperature, 42 g of dimethylacetylenecarbinol, obtained

by the method of A. E. Favorsky, by condensation of acetylene with acetone over powdered KOH, was added. After addition of the dimethylacetylenecarbinol, the reaction mixture was mixed again for a period of 1 hour, after which, also without chilling, 50 g of chloroacetone was added. The reaction mixture stood over night, then was decomposed by 30% acetic acid. After suitable treatment and distillation, 53 g (60% based on the amount of dimethylacetylenecarbinol taken) of chloroglycols, the constants of which are presented in Table 1, were obtained. The substance was a viscous, slightly yellow liquid.

0.0877, 0.0918 g sub.: 23.6, 24.8 ml CH_4 (13°, 751 mm). 0.1428, 0.1523 g sub.: 0.1150, 0.1219 g AgCl. Found %: active H 1.137, 1.132; Cl 19.92, 19.80. $C_8H_{13}O_2Cl$. Calculated %: active H 1.141; Cl 20.08.

TABLE 4

Compound No.	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
(X)		46-47° (2)	1.5493	0.9976	44.09	43.47
(XI)		65-66 (3)	1.5513	0.9981	48.90	48.08
(XII)		66-67 (2)	1.5418	0.9850	48.59	48.08

2. Production of 2,5-dimethyloxido-1,2-hexin–3-ol-5 (IV). 50 g of chloro-2,5-dimethyl-hexine-3-diol-2,5 dissolved in 300 ml of anhydrous ether, was placed in a flask with reflux condenser. Gradually, 40 g of powdered caustic potash was poured in, in small portions. The ether layer was decanted, the precipitate was dissolved in water, and extracted with ether. The ether solution and the extract were dried over Na_2SO_4. After distillation in vacuo, 35 g of the oxide, the constants of which are given in Table 2, was separated. The yield was 89%.

0.0643, 0.1022 g sub.: 11.0, 17.1 ml CH_4 (12.5°, 748.3 mm). 0.1015, 0.1058 g sub.: 0.2543, 0.2646 g CO_2; 0.0797, 0.0837 g H_2O. Found %: active H 0.716, 0.700; C 68.38, 68.25; H 8.79, 8.85. $C_8H_{12}O_2$. Calculated %: active H 0.719; C 68.54; H 8.63.

3. Production of chloro-2,5-dimethyl-heptine-3-diol-2,5 (II). The chloroglycol was obtained, just as for (I), without chilling the reaction mixture. For 1 mole of ethyl magnesium bromide, 50 g of methylethyl acetylenecarbinol and 50 g of chloroacetone were taken. The organo-magnesium complex was treated in the usual way. For determining the chloroglycols, part of the ether solution was used. The ether was removed, and the remaining material was distilled in vacuo. A viscous substance, the constants of which are presented in Table 1, was formed.

0.0918 g sub.: 22.2 ml CH_4 (13.5°, 767 mm). 0.0965 g sub.: 22.9 ml CH_4 (13°, 768.5 mm). 0.1821, 0.1582 g sub.: 0.1353, 0.1178 g AgCl. Found %: active H 1.033, 1.018; Cl 18.38, 18.42. $C_9H_{15}O_2Cl$. Calculated %: active H 1.082; Cl 18.60.

4. Production of 2,5-dimethyloxido-1,2-heptin–3-ol-5 (V). The dried ether solution of chloroglycols, obtained after decomposition of the organo-magnesium complex, was treated with powdered KOH. After distillation in vacuo, 38 g of oxide and 14 g of unreacted methylethylacetylenecarbinol were obtained. Calculated on the basis of the reacted methylethylacetylenecarbinol, the oxide yield amounted to 92%. The constants are given in Table 2.

0.0882, 0.0991 g sub.: 13.6, 15.5 ml CH_4 (13°, 768.5 mm). 0.1087, 0.1012 g sub.: 0.2786, 0.2591 g CO_2; 0.0904, 0.0865 g H_2O. Found %: active H 0.661, 0.671; C 69.95, 69.87; H 9.31, 9.33. $C_9H_{14}O_2$. Calculated %: active H 0.654; C 70.10; H 9.15.

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* Possibly two isomers.

5. Production of 2-chloro-3,6-dimethyl-heptine-4-diol-3,6 (III). For the synthesis, 2-chlorobutanone-3 and dimethylacetylenecarbinol were used. The chloroglycol was synthesized in the same way as was the preceding. For 1 mole of ethyl magnesium bromide, 50 g of dimethylacetylenecarbinol and 50 g of chloromethylethylketone were used. After treatment of the organo-magnesium complex, the separation of the chloroglycol in the pure form was not successful, since it decomposed on distillation in vacuo at 2 mm.

6. Production of 3,6-dimethyl-oxido-2,3-heptin-4-ol-6 (VI). The dried ether solution of the chloroglycol, after decomposition of the organo-magnesium complex, was treated with powdered KOH. After removal of the ether, the substance was distilled in vacuo. We obtained 48 g of oxide, which amounted to 67%, based on the amount of chloromethylethylketone taken. The physical constants are presented in Table 2.

0.1144, 0.1062 g sub.: 17.0, 16.5 ml CH_4 (13°, 760 mm). 0.1052, 0.1035 g sub.: 0.2694, 0.2647 g CO_2; 0.0872, 0.0852 g H_2O. Found %: active H 0.630, 0.659; C 69.89, 69.81; H 9.28, 9.21. $C_9H_{14}O_2$. Calculated %: active H 0.654; C 70.10; H 9.15.

7. Production of 2-(α-hydroxyisopropyl)-4-methylthiophene (VII). In a round-bottomed flask fitted with a mechanical stirrer we placed 20 g of $Ba(OH)_2$ and 150 ml of water. Hydrogen sulfide was passed into the solution for 30 minutes, after which 35 g of 2,5-dimethyloxido-1,2-hexin-3-ol-5 was added dropwise. The temperature of the reaction mixture rapidly rose to 60°. Addition of the oxide was regulated so that the temperature did not exceed 60°. After addition of all the oxide, hydrogen sulfide was passed in again for a period of 1 hour. Then the reaction mixture was acidified with the calculated amount of acetic acid, and extracted with ether. The ether solution was dried over Na_2SO_4, the ether was removed, and the remaining material was distilled in vacuo. We obtained 31 g of product, which amounted to 79% of the theoretical. The hydroxythiophene quickly crystallized in a vessel; that which was recrystallized from ligroin melted at 47-48°. With isatin in concentrated sulfuric acid, it gave a dark reddish-violet color. With mercury acetate, it formed a yellow precipitate, which decomposed at 230° without melting. On standing, water was liberated, and the substance was converted to a brown liquid.

0.1015, 0.1031 g sub.: 15.7 ml CH_4 (13.5°, 751.8 mm). Found %: active H 0.647, 0.637. $C_8H_{12}OS$. Calculated %: active H 0.645.

8. Production of 2-isopropylene-4-methylthiophene (X). 5 g of hydroxythiophene (VII) was heated with 100 ml of 10% sulfuric acid. The dehydration product was distilled with steam, extracted with ether, and dried over calcined potash, the ether was removed, and the substance was distilled in vacuo. The physical constants are given in Table 4.

0.2317, 0.2531 g sub.: 0.3944, 0.4292 g $BaSO_4$. Found %: S 23.38, 23.29. $C_8H_{10}S$. Calculated %: S 23.20.

9. Production of 2-(α-hydroxy-sec. butyl)-4-methylthiophene (VIII). It was obtained just as was the preceding substance. We used 20 g of $Ba(OH)_2$, 150 ml of water, and 32 g of 2,5-dimethyloxido-1,2-heptin-3-ol-5. The addition of the oxide was regulated so that the temperature of the reaction mixture did not exceed 50°. After treatment, as described above, and distillation, we obtained 28 g of hydroxythiophene, which amounted to 80%. With isatin sulfate, it gave a dark-red color. The constants are presented in Table 3.

0.1048 g sub.: 13.9 ml CH_4 (10.5°, 768.3 mm). 0.0990 g sub.: 14.5 ml CH_4 (13°, 767.5 mm). 0.2621, 0.2738 g sub.: 0.3545, 0.3722 g $BaSO_4$. Found %: active H 0.577, 0.627; S 18.58, 18.67. $C_9H_{14}OS$. Calculated %: active H 0.592; S 18.84.

10. Production of 2-(α-methylpropenyl)-4-methylthiophene (XI). 16 g of hydroxythiophene (VIII) was heated to boiling with a 10% solution of H_2SO_4. After distillation with steam, the dehydration product was extracted with ether. We obtained 10.5 g of the substance, which amounts to 72% of the theoretical. The physical constants are given in Table 4.

0.1982, 0.2313 g sub.: 0.3020, 0.3505 g $BaSO_4$. Found %: S 20.93, 20.81. $C_9H_{12}S$. Calculated %: S 21.06.

11. Production of 2-(α-hydroxypropyl)-4,5-dimethyl-thiophene (IX). It was produced as described above. We used 30 g of 3,6-di methyl-hydroxy-2,3-heptin-4-ol-6. . We obtained 21 g (63%) of hydroxythiophene. The constants are given in Table 3.

0.1117, 0.1025 g sub.: 15.3, 15.1 ml CH_4 (13°, 758.2 mm). 0.2100, 0.2431 g sub.: 0.2812, 0.3294 g $BaSO_4$. Found %: active H 0.580, 0.609; S 18.39, 18.61. $C_9H_{14}OS$. Calculated %: active H 0.592; S 18.84.

12. Production of 2-isopropenyl-4,5-dimethylthiophene (XII). Dehydration of (IX) was carried out with 10% H_2SO_4 as described above. The physical constants of the compound obtained are given in Table 4.

0.1821, 0.2013 g sub.: 0.2775, 0.3055 g $BaSO_4$. Found %: S 20.94, 20.85. $C_9H_{12}S$. Calculated %: S 21.06 .

SUMMARY

1. By reaction of dimethylacetylenecarbinol and methylethylacetylenecarbinol with chloroacetone and 2-chlorobutanone-3, according to the method of Iotsich, we carried out for the first time, the synthesis of the following compounds: chloro-2,5-dimethylhexine-3-diol-2,5, chloro-2,5-dimethyl-heptine-3-diol-2,5 and 2-chloro-3,6-dimethyl-heptine-4-diol-3,6.

2. The acetylenic chloroglycols treated with powdered KOH gave the following γ-hydroxyalcohols: 2,5-dimethyloxido-1,2-hexin-3-ol-5, 2,5-dimethyloxido-1,2-heptin-3-ol-5 and 3,6-dimethyloxido-2,3-heptine-4-ol-6.

3. By reaction of the above-mentioned oxides with hydrogen sulfide in the presence of $Ba(OH)_2$, we synthesized the following hydroxyalkylthiophenes: 2-(α-hydroxyisopropyl)-4-methylthiophene, 2-(α-hydroxy-sec. butyl)-4-methylthiophene and 2-(α-hydroxyisopropyl)-4,5-dimethylthiophene.

4. By dehydration of the hydroxyalkylthiophenes with dilute sulfuric acid, we obtained the following vinylthiophenes: 2-isopropyl-4-methylthiophene, 2-(α-methylpropenyl)-4-methylthiophene and 2-isopropenyl-4,5-dimethylthiophene. The synthesis of all the compounds listed above was carried out for the first time.

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* See Consultants Bureau Translation, pages 1017, 1649.

[illegible] 0.9815 g [illegible] g subst.: [illegible]. Calculated %: [illegible]

SUMMARY

1. By reaction of dimethylacetylenylcarbinol and methylethylacetylenylcarbinol with chloroacetone and 1-chlorobutanone-2, according to the method of Favorskii, we carried out for the first time, the synthesis of the following compounds: [illegible]

2. The acetylenic chlorohydrins treated with powdered KOH gave the following [illegible]

3. By reaction of the above-mentioned oxides with [illegible] we synthesized the following hydroxyalkylfuranones: [illegible]

4. By dehydration of the hydroxyalkylfuranones with [illegible] we obtained the following [illegible]. The synthesis of all the compounds listed above was carried out for the first time.

LITERATURE CITED

[1] [illegible], J. Gen. Chem. [illegible]

[2] [illegible], Ber. [illegible]

[3] [illegible], J. Am. Chem. Soc. [illegible]

[4] [illegible], J. Am. Chem. Soc. [illegible]

[5] [illegible], Ann. [illegible]; [illegible], J. Am. Chem. Soc. [illegible]

[6] [illegible], J. Gen. Chem. [illegible]

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* See Consultants Bureau Translation, page 1017.

SYNTHESIS OF DIACETYLENIC GLYCOLS IN THE PRESENCE OF Cu_2Br_2

A. I. Nogaideli and R. Shvangiradze

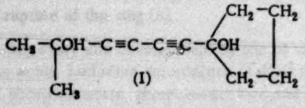
It is well-known that Yu. S. Zalkind and his students were the first to use cuprous polychloride as a condensing agent for the production of diacetylenic derivatives [1].

Our experiments showed that cuprous polybromide is a better condensing agent than Cu_2Cl_2, for mono-substitution of the acetylenecarbinols. The advantages of Cu_2Br_2 include the fact that a more uniform condensation product is obtained from the reaction. On condensation of dimethylacetylenecarbinol in the presence of cuprous polybromide, a quantitative yield of 2,7-dimethyl-octadiene-3,5-diol-2,7 was obtained.

We also used Cu_2Br_2 for the synthesis of diacetylene glycols of asymmetrical structures. Similar diacetylene glycols were not known.

It was shown that by reacting an equimolecular mixture of dimethylacetylene- and cyclopentylacetylenecarbinol, a diacetylene glycol of asymmetrical structure – 2-methyl-6-(1'-hydroxycyclopentyl)-hexadien-3,5-ol-2, having a m.p. of 105-107°, was obtained in a yield of 80-85%. Another glycol having a m.p. of 124-127° also was obtained in small quantity.

Thus, of the three possible glycols from this reaction, the glycol of asymmetrical structure (I) formed.



(I)

Further investigation showed that this reaction could also be carried out using other carbinol homologs.

EXPERIMENTAL

1. Condensation of dimethylacetylenecarbinol in the presence of Cu_2Br_2. To a reaction mixture consisting of 66.8 g of NH_4Cl, 33 g of Cu_2Br_2, 280 ml of H_2O and 2-3 drops of concentrated hydrochloric acid, in a three-necked flask, 10 g of dimethylacetylenecarbinol was added dropwise, with constant stirring and bubbling in of air. The mixture was heated to 40-50°. After 30-40 minutes, white crystals began to precipitate in the clear solution. A total of 9.6 g (97.4 %) of crystals (from benzene) having a m.p. of 130-131° was obtained.

2. Synthesis of 2-methyl-6-(1'-hydroxycyclopentyl)-hexadien-3,5-ol-2. A mixture of 59.8 g of NH_4Cl, 29.8 g of Cu_2Br_2 and 240 ml of water was used for the reaction; 2-3 drops of concentrated hydrochloric acid was added. With constant stirring, a mixture of 4 g of dimethylacetylenecarbinol and 5.2 g of cyclopentylacetylenecarbinol was added dropwise.

The precipitate (9.2 g) was recrystallized from benzene. The first portion of crystals (8.0 g) had a m.p. of 105-107°. The second portion (0.5 g) melted at 124-127°. The mixed sample melted at 114-125°.

Analysis of crystals having a m.p. of 105-107°:

0.0848 g sub.: 2.2316 g CO_2: 0.0644 g H_2O. 0.0168 g sub.: 0.12 g benzene: Δt 30°. 0.0880 g sub.: 23 ml CH_4 (18°, 722 mm). Found %: C 74.50; H 8.44; M 193. $C_{12}H_{14}(OH)_2$. Calculated %: C 75.00; H 8.33. M 192; 23 ml CH_4.

SUMMARY

1. It was found that Cu_2Br_2, as well as Cu_2Cl_2, is a good condensing agent for the production of diacetylenic glycols from mono-substituted acetylenecarbinols.

2. On reacting an equimolecular mixture of dimethylacetylene and cyclopentylacetylenecarbinol in the presence of Cu_2Br_2, we obtained for the first time a glycol of asymmetrical structure – 2-methyl-6-(1'-hydroxycyclopentyl)-hexadien–2,5-ol-2, in a yield of 85-88%.

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NEW METHOD OF SYNTHESIZING THE ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

XVII. ADDITION OF THE ESTERS OF ETHYLPHOSPHINOUS ACID, DIALKYLPHOSPHOROUS AND DIALKYLTHIOPHOSPHOROUS ACIDS TO UNSATURATED KETONES

A. N. Pudovik, R. D. Sabirova and T. A. Tener

In spite of the positive interest in them, the esters of the ketophosphinic acids, which contain ketonic and phosphinic groups connected directly to or separated from the methylene group, until now seem to have been a comparatively little studied group of the organo-phosphorus compounds. Until recently, the majority of known compounds of this type were obtained chiefly by the method of A. E. Arbuzov. The first representative ester of the ketophosphinic acids was synthesized by A. E. Arbuzov and Razumov. Reacting triethyl phosphate with bromoacetophenone, they obtained diethylphosphoneacetophenone [1]. And later on, Razumov and Petrov, by a similar method, synthesized diethylphosphoneacetone [2]. Kabachnik and Rossyskaya [3], reacting a fatty acid halide with the complete ester of phosphorous acid, obtained a ketophosphinic ester, in which the ketonic and phosphinic groups were directly connected. Using benzoyl halide instead of a fatty acid halide, Kosolapov [4] obtained the ethyl ester of benzoylphosphinic acid. A. E. Arbuzov, Zoroastrova and Rizpolozhensky studied the action of acetyl bromide on the cyclic esters of phosphorous acid. Depending on the nature of the ester group, the reaction proceeds either with preservation of, or with rupture of the ring [5].

In connection with the discovery and development by one of us of a new method of synthesizing esters of phosphinic and thiophosphinic acids, including the addition of dialkylphosphorous, dialkylthiophosphorous and phosphinous acids, and also ethyl phosphoacetate, phosphoneacetone and similar types of compounds containing a mobile hydrogen atom, to unsaturated compounds of the electrophilic type, a new, extremely simple and convenient method for the synthesis of esters of the ketophosphinic acids was proposed [6]. Essentially, the method consists of addition of dialkylphosphorous and dialkylthiophosphorous acids to α,β-unsaturated ketones. In a series of previous reports, it was shown that dialkylphosphorous and dialkylthiophosphorous acids, and also ethyl phosphonacetate, add easily and smoothly to ethylideneacetone, benzalacetone and furfuralacetone. Addition products of dialkylphosphorous and dialkylthiophosphorous acids were also formed with more complex unsaturated ketones – mesityl oxide, β,β-dimethylvinyl-β'-methoxyethyl ketone, α,β-dimethylvinyl ketone, α-methylvinyl-γ-methoxypropyl ketone and β,β-dimethyldivinyl ketone. All the addition reactions were carried out in the presence of alkali metal alcoholates. In case of the unsaturated ketones having a large number of substitution groups, the reaction proceeds sufficiently energetically, but for its accomplishment, a considerable amount of catalyst is required. The sharpest effect of substitution groups – the screening effect – appears to be the case of the addition of ethylphosphonacetate to unsaturated ketones. Even in the presence of a large amount of catalyst and with prolonged heating, we did not succeed in bringing about the addition of it to mesityl oxide and β-methyl-β-ethylvinylethyl ketone.

Continuing our earlier investigations, in the present report we have studied the addition of dialkylphosphorous and dialkylthiophosphorous acids to some new unsaturated ketones: hepten-3-one-2, 1-phenylpenten-1-one-3 and 3-methylhepten-1-one-5. Addition was carried out in the presence of alkali metal alcoholates by the method described in detail in preceding reports. The constants of the addition products, corresponding to the ketophosphinic and ketothiophosphinic esters, are presented in Table 1.

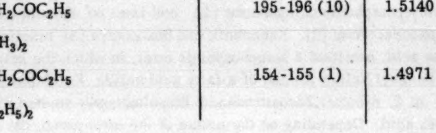
We went on to studies of the addition of the esters of ethylphosphinous acid to unsaturated ketones. The esters of aryl- and alkylphosphinous acids have become known only recently. A series of esters of phenylphosphinous acid were obtained by Kosolapov [7], Pudovik and Yarmukhametov [8], but the esters of ethylphosphinous acid were described for the first time in a report by B. A. Arbuzov and Rizpolozhensky [9]. We carried out additions of the esters of ethylphosphinous acids to ethylideneacetone, benzalacetone, benzalethylmethyl ketone, mesityl oxide and 3-methylhepten-3-one-5.

TABLE 1

Compound	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	Yield (% of the theoretical)
1	$C_3H_7CHCH_2COCH_3$ $O{=}P(OC_2H_5)_2$	139-140° (8)	1.4415	1.0234	63
2	$C_3H_7CHCH_2COCH_3$ $O{=}P(OC_4H_9)_2$	166-167 (5)	1.4450	0.9813	61
3	$C_3H_7CHCH_2COCH_3$ $S{=}P(OC_2H_5)_2$	133-134 (4)	1.4740	1.0428	42
4	$C_2H_5C(CH_3)CH_2COCH_3$ $O{=}P(OC_2H_5)_2$	124-126 (2)	1.4481	1.0308	31
5	$C_2H_5C(CH_3)CH_2COCH_3$ $S{=}P(OC_2H_5)_2$	141-143 (6)	1.4798	1.0491	62
6	$C_6H_5CHCH_2COC_2H_5$ $O{=}P(OCH_3)_2$	195-196 (10)	1.5140	1.1610	71
7	$C_6H_5CHCH_2COC_2H_5$ $O{=}P(OC_2H_5)_2$	154-155 (1)	1.4971	1.1040	61

Reaction was, as in the case of the dialkylphosphorous and dialkylthiophosphorous acids, preceded by an induction period, lasting in different cases from several seconds to several minutes, after which the reaction proceeded very rapidly, accompanied by a strong evolution of heat. Qualitatively, it was observed that an increase in the number of groups replaced by vinyl groups lengthens the time of the induction period and requires a larger amount of catalyst for completion of the reaction. For carrying out all the reactions, we used sodium alcoholate and an ester of ethylphosphinous acid, containing the same radicals in the ester group.

The reaction can be represented by the following equation:



where R = C_2H_5, n-C_4H_9; R' = H, CH_3; R'' = CH_3, C_2H_5, C_6H_5; R''' = CH_3, C_2H_5.

The constants and yields of the synthesized addition products of the corresponding esters of ketophosphinic acids are provided in Table 2.

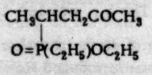
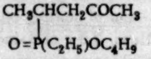
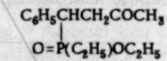
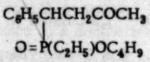
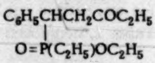
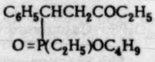
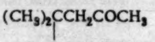
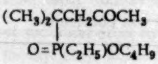
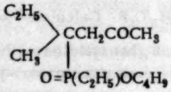
The yields of addition products of the esters of ethylphosphinous acid and unsaturated ketones were somewhat lower than for the dialkylphosphorous and dialkylthiophosphorous acids. The ketophosphinic esters obtained were colorless liquids having disagreeable odors, and were highly soluble in alcohol and ether, and partially soluble in water.

EXPERIMENTAL

Addition of Dialkylphosphorous and Dialkylthiophosphorous Acids to Unsaturated Ketones

Addition of diethylphosphorous acids to butylideneacetone. 6.3 g of butylideneacetone was added to 6 g of diethylphosphorous acid, and a saturated solution of sodium ethylate was introduced dropwise. After a short induction period, the reaction proceeded very vigorously, accompanied by a large liberation of heat. The reaction

TABLE 2

Compound	Formula	B.p. at pressure (mm)	n_D^{20}	d_4^{20}	Yield (in% of the theoretical)
1	 $CH_3\underset{O=P(C_2H_5)OC_2H_5}{\underset{\vert}{C}H}CH_2COCH_3$	139° (9)	1.4561	1.0435	63
2	 $CH_3\underset{O=P(C_2H_5)OC_4H_9}{\underset{\vert}{C}H}CH_2COCH_3$	156-157 (5)	1.4563	1.0121	50
3	 $C_6H_5\underset{O=P(C_2H_5)OC_2H_5}{\underset{\vert}{C}H}CH_2COCH_3$	178-179 (8)	1.5150	1.1084	46
4	 $C_6H_5\underset{O=P(C_2H_5)OC_4H_9}{\underset{\vert}{C}H}CH_2COCH_3$	194-196 (6)	1.5188	1.0906	44
5	 $C_6H_5\underset{O=P(C_2H_5)OC_2H_5}{\underset{\vert}{C}H}CH_2COC_2H_5$	178-180 (8)	1.5096	1.1008	48
6	 $C_6H_5\underset{O=P(C_2H_5)OC_4H_9}{\underset{\vert}{C}H}CH_2COC_2H_5$	196-198 (7)	1.5109	1.0664	47
7	 $(CH_3)_2\underset{O=P(C_2H_5)OC_2H_5}{\underset{\vert}{C}}CH_2COCH_3$	152.5 (14)	1.4577	1.0392	46
8	 $(CH_3)_2\underset{O=P(C_2H_5)OC_4H_9}{\underset{\vert}{C}}CH_2COCH_3$	154-155.5 (6)	1.4588	1.0066	36
9	 $\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\rangle\underset{O=P(C_2H_5)OC_4H_9}{\underset{\vert}{C}}CH_2COCH_3$	176-177 (11)	1.4641	1.0002	55

mixture was heated on a boiling water bath for 20 minutes, and then distilled in vacuo. As a result of two distillations, 6.9 g of 4-(dimethylphosphono)-heptanone-2 (Table 2, Compound 1) was formed.

MR_D 64.55; calculated 63.87.

0.1300, 0.1352 g sub.: 29.7, 30.8 ml NaOH (T = 0.01962). Found %: P 12.26, 12.32. $C_{11}H_{23}O_4P$. Calculated %: P 12.40.

Addition of dibutylphosphorous acid to butylideneacetone. The reaction was carried out with 9.7 g of dibutylphosphorous acid and 6.3 g of butylideneacetone in the presence of sodium butylate. The method of carrying out the reaction was similar to that described in the preceding experiment. 9.2 g of 4-(dibutylphosphono)-heptanone-2 and a series of low-boiling fractions (Table 1, compound 2) were formed.

MR_D 82.86; calculated 82.35.

0.1498, 0.1733 g sub.: 28.8, 33.8 ml NaOH (T = 0.01962). Found %: P. 10.48. $C_{15}H_{31}O_4P$. Calculated %: P 10.13.

Addition of diethylthiophosphorous acid to butylideneacetone. 5.1 g of diethylthiophosphorous acid and 3.7 g of butylideneacetone were used in the reaction. The reaction was carried out in the presence of sodium ethylate. As a result of 2 distillations of the reaction mixture, 3.7 g of 4-(diethylthiophosphono)-heptanone-2 (Table 1, compound 3) was obtained.

MR_D 71.69; calculated 71.36.

0.1233 g sub.: 27.6 ml NaOH (T = 0.01962). Found %: P 12.03. $C_{11}H_{23}O_3PS$. Calculated %: P 11.65.

Synthesis of 3-methylhepten - 3-one-5. In a round-bottomed flask, fitted with a mechanical stirrer and a reflux condenser, 200 ml of dry methyl ethyl ketone and 50 g of finely-ground calcium carbide were placed. The reaction mixture was heated on a water bath, with stirring, for 10 hours. Then the calcium carbide and the lime that formed were filtered off, the acetone was distilled from the filtrate, and the residuals were distilled through a visual measuring column. The yield of ketone amounted to 25-30%. The b.p. was 163-165°.

Addition of diethylphosphorous acid to 3-methylhepten - 3-one-5. 6.1 g of diethylphosphorous acid was added to 6.5 g of 3-methylhepten—3-one-5, and a solution of sodium ethylate was introduced slowly by drops. A strong evolution of heat from the reaction mixture was observed. After a half-hour of heating on a boiling water bath, the reaction mixture was distilled in vacuo. As a result of 2 distillations, 3.6 g of 5-methyl-5-(diethylphosphono)-heptanone-3 (Table 1, compound 4) was obtained. A large resinous residue was observed in the flask after the distillation.

MR_D 68.56; calculated 68.48.

0.1368 g sub.: 30.3 ml NaOH(T = 0.01962). Found %: P 11.91. $C_{12}H_{25}O_4P$. Calculated %: P 11.74.

Addition of diethylthiophosphorous acid to 3-methylhepten - 3-one-5. 5.4 g of 3-methylhepten 3-one-5 and 6.6 g of diethylthiophosphorous acid were used for the reaction. The reaction was carried out in the presence of sodium ethylate. 7.4 g of 5-methyl-5-(diethylthiophosphono)-heptanone-3 (Table 1, compound 5) was obtained.

MR_D 75.83; calculated 75.98.

0.1100 g sub.: 49.0 ml NaOH (T = 0.008808). Found %: P. 10.86. $C_{12}H_{25}O_3PS$. Calculated %: P. 11.07.

Addition of dimethylphosphorous acid to benzylidene methyl ethyl ketone. The reaction was carried out with 11.7 g of benzylidene methyl ethyl ketone and 10 g of dimethylphosphorous acid in the presence of sodium methylate. The reaction proceeded very energetically, accompanied by a strong evolution of heat. After heating for 20 minutes on a boiling water bath, the reaction mixture was distilled in vacuo. After 2 distillations, 14.2 g of 1-phenyl-1-(dimethylphosphono)-pentanone-3 (Table 1, compound 6) was obtained.

MR_D 69.99; calculated 69.49.

0.1330 g sub.: 63.8 ml NaOH (T = 0.008808). Found %: P 11.69. $C_{13}H_{19}O_4P$. Calculated %: P 11.49.

Addition of diethylphosphorous acid to benzylidene methyl ethyl ketone. 8 g benzylidene methyl ethyl ketone, 6.9 g of diethylphosphorous acid were used in the reaction. 9 g of 1-phenyl-1-(diethylphosphono)-pentanone-3 (Table 1, compound 7) was isolated.

MR_D 79.00; calculated 78.71.

0.1010 g sub.: 19.5 ml NaOH (T = 0.01962). Found %: P 10.36. $C_{15}H_{23}O_4P$. Calculated %: P 10.40.

Addition of Esters of Ethylphosphinous Acid to Unsaturated Ketones

Addition of the ethyl ester to ethylideneacetone. To a mixture of 6.3 g of the ethyl ester of ethylphosphinous acid and 4.4 g of ethylideneacetone, placed in an Arbuzov flask, a saturated solution of sodium ethylate was introduced slowly by drops. The reaction proceeded very readily, accompanied by a strong evolution of heat. A total of about 15 drops of ethylate was added. After heating for 1 hour on a boiling water bath, the reaction mixture was distilled in vacuo. As a result of 2 distillations, 6.8 g of 2-(ethoxyethylphosphinoxido)-pentanone-4 (Table 2, compound 1) was obtained.

MR_D 53.67; calculated 52.99.

0.1460, 0.2187 g sub.: 88.6, 162.2 ml NaOH (T = 0.008808). Found %: P. 14.74, 14.82. $C_9H_{19}O_3P$. Calculated %: P 15.05.

Addition of the butyl ester to ethylideneacetone. 4.5 g of ethylideneacetone and 8 g of the n-butyl ester of ethylphosphinous acid were used in the reaction. For carrying out the reaction, 30 drops of a saturated solution of sodium butylate were added to the reaction mixture. As a result of distillation of the reaction mixture, the following fractions were obtained: 1st, b.p. 36-110° (7 mm), 5.6 g; 2nd, b.p. 143-154° (7 mm), 4.6 g. As a result of distillation of the 2nd fraction, 2-(butoxyethylphosphinoxido)-pentanone-4 (Table 2, compound 2) was obtained.

Bromination of the addition product, according to McIlliney showed the absence of a double bond.

MR_D 62.88; calculated 62.23.

0.1274 g sub.: 68.1 ml NaOH (T = 0.008808). Found %: P 13.03. $C_{11}H_{23}O_3P$. Calculated %: P 13.25.

Addition of the ethyl ester to benzylideneacetone. To a mixture of 5 g of the ethyl ester of ethylphosphinous acid and 5.6 g of benzylideneacetone, about 20 drops of a saturated solution of sodium ethylate was added slowly. After a brief heating on the water bath and distillation in vacuo, 4.8 g of a fraction having a b.p. of 150-178° at 8 mm was separated. By re-distillation from an Arbuzov flask fitted with a small fractionating column having an internal spiral, 4.8 g of 1-phenyl-1-(ethoxyethylphosphinoxido)-butanone-3 (Table 2, compound 3) was obtained.

MR_D 72.91; calculated 72.48.

0.1122 g sub.: 24.5 ml NaOH (T = 0.01962). Found %: P 11.85. $C_{14}H_{21}O_3P$. Calculated %: P 11.56.

Addition of the butyl ester to benzylideneacetone. The reaction was carried out with 4.3 g butyl ester and 4.1 g of benzylideneacetone in the presence of sodium butylate. 3.7 g of 1-phenyl-1-(butoxyethylphosphinoxido)-pentanone-3 (Table 2, compound 4) was isolated. Bromination of the addition product, according to McIlliney, showed the absence of a double bond.

MR_D 82.34; calculated 81.71.

0.1322, 0.1590 g sub.: 26.7, 32.0 ml NaOH (T = 0.01962). Found %: P 10.97, 10.93. $C_{16}H_{25}O_3P$. Calculated %: P 10.47.

Addition of the ethyl ester to benzylidene methyl ethyl ketone. 2.2 g of the ethyl ester of ethylphosphinous acid and 2.9 g of benzylidene methyl ethyl ketone were used in the reaction. 2.5 g of 1-phenyl-1-(ethoxyethylphosphinoxido)-pentanone-3 (Table 2, compound 5) was obtained.

MR_D 76.57; calculated 77.08.

0.1642 g sub.: 72.1 ml NaOH (T = 0.008808). Found %: P 10.71. $C_{15}H_{23}O_3P$. Calculated %: P 10.98.

Addition of the butyl ester to benzylidene methyl ethyl ketone. The reaction was carried out with 6.4 g of benzylidene methyl ethyl ketone and 6 g of the butyl ester of ethylphosphinous acid in the presence of sodium butylate. After an hour of heating on the water bath, the reaction mixture was distilled in vacuo. The first distillation proceeded with little indication of decomposition. The 1st fraction in the amount of 4.4 g boiled within the range 80-175° at 10 mm and the 2nd, in an amount of 5.8 g, in a range of 194-208° at 9 mm. On repeated distillations of the second fraction, 5.8 g of 1-phenyl-1-(butoxyethylphosphinoxido)-pentanone-3 Table 2, compound 6) was obtained.

MR_D 87.06; calculated 86.34.

0.1827 g sub.: 34.3 ml NaOH (T = 0.01962). Found %: P 10.21. $C_{17}H_{27}O_3P$. Calculated %: P 10.00.

Addition of the ethyl ester to mesityl oxide. For carrying out the reaction, 25 drops of a saturated solution of sodium ethylate was added to a reaction mixture consisting of 3.2 g of mesityl oxide and 4 g of ethyl ester of ethylphosphinous acid. We observed a considerable induction period, after which the reaction proceeded very energetically, with a strong evolution of heat. After heating for 1 hour on a water bath, and distilling 2 times in vacuo, 3.3 g of 2-methyl-2-(ethoxyethylphosphinoxido)-pentanone-4 (Table 2, compound 7) was obtained.

MR_D 57.73; calculated 57.61.

0.1613 g sub.: 41.1 ml NaOH (T = 0.01962). Found %: P 13.83. $C_{10}H_{21}O_3P$. Calculated %: P 14.09.

Addition of the butyl ester to mesityl oxide. For carrying out the reaction, about 50 drops of a saturated solution of sodium butylate was added to a mixture of 6.5 g of mesityl oxide and 10 g of butyl ester of ethylphosphinous acid. 6 g of 2-methyl-2-(butoxyphosphinoxido)-pentanone-4 (Table 2, compound 8) was obtained.

MR_D 67.32; calculated 66.81.

0.1405 g sub.: 31.1 ml NaOH (T = 0.01962). Found %: P 12.79. $C_{12}H_{25}O_3P$. Calculated %: P 12.50.

Addition of the butyl ester to 3-methylhepten—3-one-5. About 60 drops of a solution of sodium ethylate was added to a reaction mixture consisting of 7 g of the butyl ester of ethylphosphinous acid and 8 g of 3-methylhepten—3-one-5. The reaction was preceded by a considerable induction period. As a result of 2 distillations of the reaction mixture, 7.2 g of 3-methyl-3-(butoxyethylphosphinoxido)-hexanone-5 (Table 2, compound 9) was obtained.

MR_D 76.16; calculated 76.09.

0.1355, 0.1217 g sub.: 27.0, 25.9 ml NaOH (T = 0.01962). Found %: P 10.82, 11.56. $C_{14}H_{29}O_3P$.
Calculated %: P 11.23.

SUMMARY

1. It was shown that the esters of phosphinous acid add to unsaturated ketones in the presence of alkali metal alcoholates. We carried out the addition of the ethyl and butyl esters of ethylphosphinous acid to ethylideneacetone, benzylideneacetone, benzylidene methyl ethyl ketone, mesityl oxide and 3-methylhepten—3-one-5.

2. We obtained a series of new ketophosphinic esters by addition of diethylphosphorous, diethylthiophosphorous and dibutylphosphorous acids to hepten-3-one-2, 1-phenylpenten-1-one-3 and 3-methylhepten-3-one-5.

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*** See Consultants Bureau Translation, page 803.

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PHOSPHORYL CHLORIDE ISOCYANATE

A. V. Kirsanov

According to the scheme of Wallach-Gerhardt [1], accepted in all the handbooks and elementary textbooks of organic chemistry, the amides of the carboxylic acids react with phosphorus pentachloride with the formation of phosphoryl chloride and unstable chloroamides, which are easily decomposed, under the conditions of the reaction, to chloroimides and hydrogen chloride, and further to nitriles and hydrogen chloride, according to the scheme:

$$RCONH_2 + PCl_5 \rightarrow RCCl_2NH_2 + POCl_3$$

$$RCCl_2NH_2 \rightarrow HCl + RCCl{=}NH$$

$$RCCl{=}NH \rightarrow HCl + RCN.$$

Forming in some cases are the phosphorus-containing compounds of the composition, $RCONPCl_3$, which, in the opinion of Wallach, are produced according to the scheme:

$$RCCl{=}NH + POCl_3 \rightarrow HCl + RCCl{=}NPOCl_2$$

If the Wallach scheme is correct, and is of a general character, then by the reaction of urethan with phosphorus pentachloride, phosphoryl chloride and the ethyl ester of the chloramide of carbonic acid, $C_2H_5OCCl_2NH_2$, should be the first reaction products. The latter should be very unstable, and after liberation of two molecules of hydrogen chloride should give the ethyl ester of cyanuric acid, or after the liberation of ethyl chloride should give in turn carbamic chloride, cyanic acid and cyanuric acid:

$$NH_2COOC_2H_5 \xrightarrow{+\ PCl_5} NH_2CCl_2OC_2H_5 \xrightarrow[-2HCl]{} NCOC_2H_5 \rightarrow C_3N_3(OC_2H_5)_3.$$

$$NH_2CCl_2OC_2H_5 \xrightarrow{-C_2H_5Cl} NH_2COCl \xrightarrow[-HCl]{} NHCO \rightarrow C_3N_3(OH)_3.$$

The reactions of phosphorus pentachloride with urethan were studied by Folin in 1897 [2]. Without any experimental basis, Folin asserted that the reaction proceeds according to the Wallach scheme, i.e., that the first reaction products are phosphoryl chloride and the ethyl ester of the chloroamide of carbonic acid. Folin reported that, from the reaction, ethyl chloride and a "liquid which might contain carbamic chloride are formed."

Folin did not demonstrate the formation of phosphoryl chloride by the reaction of urethan with phosphorus pentachloride and, in spite of this, he considered that the study of the reaction was extremely hampered by the separation of phosphoryl chloride, which was very difficult to remove from the region of the reaction; therefore, he gave up further study of the reaction. Thus, unwarranted confidence in the correctness of the Wallach scheme led Folin to an erroneous conclusion and even forced him to give up further study of the reaction.

Experimental study of the reaction of phosphorus pentachloride with urethan showed that the reaction proceeds, not according to the scheme of Wallach, but according to the scheme of the analogous reaction of phosphorus pentachloride with an amide of a sulfo acid [3].

Phosphorus pentachloride readily reacts with urethan, in the proportion of 1 mole to 1 mole, with a large evolution of heat even at 0°. At + 10° the reaction proceeds at a greatrrate, and is completed within several hours. On rapidly diluting the reaction mixture, the energetic separation of hydrogen chloride, in the amount of 2 moles per 1 mole of urethan, proceeded with a yield of about 95%.

The fact that phosphoryl chloride and ethyl chloride did not form, was strictly demonstrated by a special experiment carried out in a vacuum of 1.0 mm, in a vessel cooled to −80°. Consequently, the reaction does not proceed according to the Wallach scheme, but proceeds as in the case of the reaction of phosphorus pentachloride with the amide of a sulfo acid [3], i.e., according to the scheme:

$$C_2H_5OCONH_2 + PCl_5 \rightarrow 2HCl + C_2H_5OCON{=}PCl_3.$$

The reaction product, obtained in a yield of about 100%, was a colorless, transparent liquid, with a d of 1.48 at 15° and a fishy odor, and it reacted vigorously with water, alcohols, phenol, ammonia, amines and carboxylic acids. On cooling to −80° the substance thickened, but did not crystallize. The elementary composition, according to the chlorine and phosphorus contents and according to titration of the hydrolysis products, corresponds quite accurately to the formula $C_3H_5O_2NPCl_3$.

According to the molecular weight obtained, the composition of the reaction product should involve the structure $C_2H_5OCON{=}PCl_3$, i.e., is the ethyl ester of trichlorophosphazocarbonic acid.

The structure,

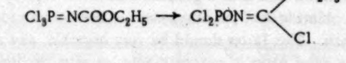
$$C_2H_5OCCl{=}NPOCl_2,$$

is also possible, but less probable.

At a temperature of + 15°, the ethyl ester of trichlorophosphazocarbonic acid is entirely stable, but at + 20° it begins to dissociate slowly, with evolution of heat and formation of ethyl chloride and phosphoryl chloride isocyanate, according to the scheme:

$$Cl_3P{=}NCOOC_2H_5 \rightarrow C_2H_5Cl + Cl_2PON{=}C{=}O.$$

The possibility (see above) of a preliminary isomerization according to the scheme:



$$Cl_3P{=}NCOOC_2H_5 \rightarrow Cl_2PON{=}C\begin{matrix}OC_2H_5\\Cl\end{matrix}$$

is not excluded.

On rapid heating to 45-50° this process proceeded explosively; therefore, for the production of phosphoryl chloride isocyanate, especially in large quantities, it is necessary to adhere to a strict temperature regime, as described in the experimental part. On violating this strict regime by accelerating the increase of the temperature of the reaction mixture, very strong and hazardous explosions are possible during the experimental study of a reaction, for which the mechanism and character of the process has still not been established.

At 30-40° the thermal cleavage of the ethyl ester of trichlorophosphazocarbonic acid proceeds entirely smoothly and safely.

The structure of the reaction product, as for phosphoryl chloride isocyanate, Cl_2PONCO, was established on the basis of the scheme of its formation (yield about 90%), the composition, molecular weight, physical (boiling point) and chemical properties, and also the composition and properties of the products of its reaction with alcohols and other compounds.

For the compound of the present composition, the structure of N-carboxyliminometaphosphoryl chloride, $ClPO{=}NCOCl$, is theoretically possible, but this structure is not very probable, since the monomolecular compound in which phosphorus is joined to two double bonds probably does not exist, and moreover, the reaction product r readily adds alcohols without liberating hydrogen chloride, which is well-accounted for only by the isocyanate structure.

Phosphoryl chloride isocyanate is a colorless, transparent liquid with a very unpleasant odor, a specific gravity of d 1.649 at 15°, n_D^{15} 1.470, having a b.p. of 136-138° at 760 mm with little decomposition. In a vacuum of 5 mm the acid chloride distills at 19.7-20.0°.

Phosphoryl chloride isocyanate is unusually reactive and enters readily into reactions with water, alcohols, amines, phenols, carboxylic acids, etc.. In the majority of cases, the reaction proceeds in two stages — at first there is addition to the isocyane-group, with formation of the acid chloride of the corresponding urethanphosphoric acid, for example according to the scheme:

$$Cl_2PONCO + CH_3OH \rightarrow Cl_2PONHCOOCH_3.$$

and then the reaction proceeds on the halogen atom, with formation of the corresponding derivative of phosphoric acid, for example:

$$Cl_2PONHCOOCH_3 + 2CH_3ONa \rightarrow (CH_3O)_2PONHCOOCH_3.$$

Thus, phosphoryl chloride isocyanate is a valuable starting material for obtaining diverse new types of derivatives of phosphoric acid.

The reaction of urethan with phosphorus pentachloride showed that the Wallach scheme for the interaction of phosphorus pentachloride with amides of the carboxylic acids, is at least not of an ordinary nature.

EXPERIMENTAL

Production of the Ethyl Ester of Trichlorophosphazocarbonic Acid

A several-liter, round-bottomed flask was connected directly to a trap cooled to −80°, to a Tishchenko bottle containing concentrated sulfuric acid, and to an absorber for hydrogen chloride containing about 0.5 liter of water. In the flask, 0.3 mole of phosphorus pentachloride (not containing phosphoryl chloride) and 0.3 mole of carefully dried urethan were placed. The mixture was stirred by hand, and the flask was immersed directly in a water bath, and heated to + 10°. At the beginning of the reaction, the bath served for heating the mixture, since the reaction is accompanied by considerable absorption of heat, and later it served for cooling the mixture, since at room temperature the reaction product slowly decomposes. After several minutes, the mixture was diluted and the energetic liberation of hydrogen chloride began, and it intensified on agitation. Gradually the liberation of hydrogen chloride abated. After 24 hours, the apparatus was dismantled, and its individual parts were weighed. The gain in weight of the trap for ethyl chloride was 0.03 g, the gain in weight of the Tishchenko bottle was 0.10 g, the yield of the main reaction product was 72.2 g, i.e., 107.3%, which is accounted for by the large quantity of hydrogen chloride dissolved in it. The apparatus was assembled again, but instead of water in the trap for hydrogen chloride, a measured amount of a 2 N solution of sodium hydroxide was placed in it, and a vacuum was gradually created. The reaction product "boiled up" and the hydrogen chloride was absorbed by the alkali, which was observable by the "current" in the trap containing the sodium hydroxide. After 2 hours, after establishing a vacuum of 10 mm, the apparatus was dismantled. The total amount of hydrogen chloride separated (according to titration) was 0.57 equiv., i.e., 95%. There was no gain in weight of the trap (−80°); consequently, the reaction product did not contain phosphoryl chloride. The yield of reaction product was 65.6 g (97.4%).

Found %: Cl 46.81, 46.91; P 13.94, 14.08. Weight equivalent of acid by hydrolysis (by boiling) 4.96, 4.91. M (in benzene) 205.0, 212.0. $C_3H_5NPCl_3O_2$. Calculated %: Cl 47.42; P 13.84. Equivalent weight of acid by hydrolysis 5.00. M 224.44.

The ethyl ester of trichlorophosphazocarbonic acid was a colorless, transparent liquid, having a d of 1.48 at 15° and a fishy odor. On mixing it with ice water, a reaction began relatively smoothly after several seconds. At room temperature, its reaction with water, as with alcohols, ammonia, and amines, proceeded very violently. During storage of the preparation at room temperature in a securely sealed vessel, a pressure is created as a result of the gradual decomposition of the substance with the formation of ethyl chloride. By rapidly heating a small quantity of the preparation to 60°, a violent effervescing occurs, and the temperature of the liquid increases to 100° because of the heat of reaction. On cooling to −80°, the ethyl ester of trichlorophosphazocarbonic acid became viscous, but did not crystallize.

In order to demonstrate that phosphoryl chloride did not form during the reaction, several experiments were carried out at 15° in a vacuum of 1.0 mm. Under these conditions, any phosphoryl chloride forming should be vaporized immediately and condensed in the trap (−80°). From the charge, consisting of 0.5 mole of phosphorus pentachloride and urethan, a gain in weight of the trap (−80°) was no more than 0.2 g, which undoubtedly may be accounted for by the seepage of moisture from the air into the reaction mixture, during the addition of urethan to the phosphorus pentachloride. Thus, it may be considered as demonstrated that phosphoryl chloride, and consequently, also the ethyl ester of the amidochloride of carbonic acid did not form during the action of phosphorus pentachloride on urethan, and that the primary reaction products were only hydrogen chloride and the ethyl ester of trichlorophosphazocarbonic acid.

Production of Phosphoryl Chloride Isocyanate

A one-liter, round-bottomed flask was connected directly to a Tishchenko bottle containing concentrated sulfuric acid, and to a trap for hydrogen chloride containing 0.8 liter of water. In the flask, 1.0 mole of phosphorus pentachloride and 1.0 mole of urethan were placed, the mixture was stirred by hand, and the flask was immersed in the water bath, and heated to + 10°. After 45 minutes, we began to heat the bath at such a rate that the temperature of 50° was reached. After this, we heated it at a rate of 1° every 2 minutes, until a temperature of 80° was attained, and the liberation of ethyl chloride did not cease. Thus, the heating required about 5.5 hours. The rate of liberation of hydrogen chloride and ethyl chloride was controlled by the bubbling in the Tishchenko bottle. The most energetic hydrogen chloride evolution was at 15-20°, and the most energetic ethyl chloride evolution was at 30-40°. By maintaining a given rate, the reaction was carried out entirely safely. On more rapid heating, ethyl chloride was liberated at an explosive rate. Thus, for example, on heating a charge of 0.2 mole for 20 minutes at 60°, a strong explosion resulted. In another case, for a charge of 0.3 mole in a 0.5 liter flask, the temperature was raised to 35° for 20 minutes, and then to 45° for 10 minutes. The reaction proceeded very violently and, therefore, the flask was drenched with a strong jet of cold water. In spite of this, after several seconds a strong explosion resulted in a bluish blaze, and the flask was shattered into small fragments, although it was vented through the Tishchenko bottle by a tube of about 8 mm diameter.

In a number of experiments, a trap for ethyl chloride, cooled to −80°, was placed between the flask and the Tishchenko bottle. On completion of the experiments, from 58.0 to 60.2 g (89.0-93.3%) of ethyl chloride had collected in this trap. On distillation from a 300 mm-long branched column, with the temperature of the outside air at −5°, we obtained from 49.2 to 50.7 g of pure ethyl chloride (76.3-78.5%) having a b.p. of 10-12°.

In several experiments, the quantity of hydrogen chloride liberated was determined by titration, by which from 1.98 to 2.02 equivalent weights of HCl, i.e., 99-101%, was found.

The yield of crude phosphoryl chloride isocyanate was 173.1-177.0 g (108.2-110.8%). For purification, the product was distilled in vacuo from a 200 mm-long branched column (temperature of the external air was + 10°) and the vessel was cooled to −20°. From a rapid distillation at 5 mm, a 20-24° fraction was collected. On very slow distillation at 5 mm, the product completely distilled at 19.7-20.0°. The yield of pure phosphoryl chloride isocyanate was 139.1-145.2 g (87.1-90.8%).

d_4^{15} 1.649; n_D^{15} 1.470.

Found %: P 19.23, 19.32; Cl 44.21, 44.21. Equivalent weight of acid by hydrolysis (by boiling) 3.94, 3.91. M 155.0, 152.7 (in benzene). CO_2NPCl_2. Calculated %: P 19.37; Cl 44.34. Equivalent weight of acid by hydrolysis 4.00. M 159.92.

The phosphoryl chloride isocyanate was a colorless, transparent liquid with a disagreeable fishy odor. Its properties are discussed in the general part of the report. After distillation of the phosphoryl chloride isocyanate, a viscous, colorless, non-crystallizing liquid, in the amount of 18-21 g, remained in the flask, but it has not as yet been investigated.

SUMMARY

1. The reaction of phosphorus pentachloride with urethan proceeded with formation of the ethyl ester of trichlorophosphazocarbonic acid.

2. The ethyl ester of trichlorophosphazocarbonic acid was almost quantitatively decomposed at 30-40° to ethyl chloride and phosphoryl chloride isocyanate.

3. Some physical and chemical properties of phosphoryl chloride and the ethyl ester of trichlorophosphazocarbonic acid were described.

4. It was shown that the Wallach scheme for the reaction of phosphorus pentachloride with the amides of carboxylic acids, is not of a general nature.

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* See Consultants Bureau Translation, page 329.

THE MOBILITY OF THE DIETHYLAMINO GROUP

1. THE REAMINATION OF BENZYLDIETHYLAMINE

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The base, benzyldiethylamine, and also quaternary ammonium salts containing the benzyl group, enter into reaction with a series of compounds, splitting off dialkylamines [1-6]. However, until the present time, data on the reaction of benzyldiethylamine with the aromatic amines were lacking in the literature, and there also were no data regarding the effect of different substituents on the course of this reaction.

TABLE

N-(Benzyl)-aniline

No.	Name of compound	B.p. of the base	M.p. of the base	Yield (%)	Results of analysis
1	N-(benzyl)-aniline	149-150° at 5 mm	–	22.1 a) 56.8	Found %: N 7.93, 7.77. $C_{13}H_{13}N$. Calculated %: N 7.65.
2	N-(benzyl)-o-chloraniline.	162-163 at 4 mm	38-39°	31.0	7.007 mg sub.: 0.421 ml N_2 (24°, 730 mm). 5.477 mg sub.: 0.333 ml N_2 (24°, 730 mm). Found %: N 6.63, 6.71. $C_{13}H_{12}NCl$. Calculated %: N 6.44.
3	N-(benzyl)-m-chloraniline . . .	172-173 at 3 mm	Hydrochloride 171-172	29.7	6.295 mg sub.: 0.323 ml N_2 (25°, 724 mm). 6.953 mg sub.: 0.362 ml N_2 (26°, 722 mm). Found %: N 5.59, 5.63. $C_{13}H_{13}NCl_2$. Calculated %: N 5.51.
4	N-(benzyl)-p-chloraniline	178 at 4 mm	45	26.4	Found %: N 6.57, 6.61. $C_{13}H_{12}NCl$. Calculated %: N 6.44.
5	N-(benzyl)-p-anisidine.	197 at 4 mm	51	30.6	Found %: N 6.42, 6.54. $C_{14}H_{15}ON$. Calculated %: N 6.57.
6	N-(benzyl)-m-nitroaniline	223-224 at 3 mm	106	8.8	Found %: N 12.63, 12.56, $C_{13}H_{12}O_2N_2$. Calculated %: N 12.28.
7	N-(benzyl)-o-toluidine.	173-174 at 7 mm	56	37.2 a) 39.5 b) 28.7	Found %: N 7.32, 7.02. $C_{14}H_{15}N$. Calculated %: N 7.11.
8	N-(benzyl)m-toluidine.	164-165 at 4 mm	–	35.7	Found %: N 7.05, 7.35. $C_{14}H_{15}N$. Calculated %: N 7.11.
9	N-(benzyl)-p-toluidine.	165-166 at 4 mm	–	36.1	Found %: N 6.89, 6.99. $C_{14}H_{15}N$. Calculated %: N 7.11.

We have attempted to elucidate the capacity of benzyldiethylamine to enter into reactions of reamination with different aromatic amines, namely: aniline, o-, m- and p-chloraniline, p-anisidine, m-nitroaniline, o-, m- and p-toluidine and p-aminophenol. On heating in a sealed tube for 12-13 hours at 180-185°, benzyldiethylaminohydrochloride enters into reactions with all of the enumerated amine bases, except p-aminophenol.

As a result of the reaction, a substituted N-(benzyl)-aniline and diethylamine formed. The yield of the product from the condensation with aniline amounted to 22.1%; it increased on introduction of such substituents as Cl, OCH_3 and CH_3, and decreased with the presence of the NO_2-group (see the table). It should be pointed out that the position of the substituent in chloraniline and toluidine did not exert a substantial effect on the yield, as did increasing the time of heating to 26 hours (see the table, No. 7,a).

However, the reaction of 1 mole of benzyldiethylamine hydrochloride with 2 moles of aniline led to a 2.5-fold increase of the yield of benzylaniline (see the table, No. 1,a).

Benzyldiethylamine did not react with p-aminophenol under the conditions described above: 4,4'-dihydroxydiphenylamine, together with the unreacted starting substances, was separated from the reaction mass. Such a subsidiary reaction was also observed in the experiment with m-chloraniline, , where, besides N-(benzyl)-m-chloraniline, 3,3'-dichlorodiphenylamine was separated in a small quantity. By way of example, for o-toluidine it was found that if the components are heated in a flask on an oil bath at 190-195°, the yield decreases (see the table, No. 7,b).

EXPERIMENTAL

The compounds named in the table were obtained by the following method: molar quantities of benzyldiethylamine hydrochloride (or base) and an aromatic amine base (or hydrochloride) were heated in a sealed tube for 12-13 hours at 180-185°. On cooling, the contents of the tube were treated with a 40% solution of sodium hydroxide (in this way the sharp odor of diethylamine was observed), and extracted with ether. The ether solution was washed with water, and dried over potash. The residuals, after removal of the ether, were distilled in vacuo; at first, unreacted starting materials distilled, and then the condensation product distilled. The latter, in the majority of cases, solidified on cooling with ice.

As an example, we present a description of the reaction of benzyldiethylamine with m-chloraniline.

N-(benzyl)-m-chloraniline

A mixture of 30 g of benzyldiethylamine hydrochloride (0.15 mole) and 19.5 g of m-chloraniline (0.15 mole) was heated in a tube for 12 hours at 180-185°. On cooling the contents of the tube, there was a transparent, viscous, red liquid, which was treated with a 40% solution of sodium hydroxide, and extracted with ether. The ether solution was washed with water and dried over potash. The yellow liquid remaining after removal of the ether, was distilled in vacuo. Besides unreacted starting materials, the two following fractions were collected: 1st at 172-173° (3 mm), 9.7 g, and the 2nd at 200-202° (3 mm), 1.1 g.

The 1st fraction was N-(benzyl)-m-chloraniline, and was a rather mobile, almost colorless liquid, which did not solidify on cooling. The hydrochloride, obtained by running in alcoholic HCl with the base, was crystallized from alcohol. The plates obtained had a m.p. of 171-172°. The yield of N-(benzyl)-m-chloraniline was 29.7%.

The viscous, yellow liquid, distilling at 200-202° (3 mm), was converted to the hydrochloride by heating it with a 10% solution of hydrochloric acid. The salt crystallized from dilute hydrochloric acid; the m.p. was 162-163°. According to data from analysis, this compound was 3,3'-dichlorophenylamine hydrochloride.

Found %: N 5.48, 5.23. $C_{12}H_9NCl_2 \cdot HCl$. Calculated %: N 5.10.

SUMMARY

1. Benzyldiethylamine enters into reaction with a series of aromatic amines, forming substituted N-(benzyl)-aniline and diethylamine.

2. The yield of reaction product increased when such substituents as Cl, OCH_3 and CH_3 were introduced into the aromatic amine, and decreased when the NO_2-group was present in it.

3. The position of the substituent in chloroaniline and toluidine exerted no substantial influence on the yield of the substituted N-(benzyl)-aniline.

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PREPARATION OF DIISOPROPYLPYROCARBONATE

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In the present work, the preparation of the diisopropyl ester of pyrocarbonic acid with the aid of a method worked out by us, based on the reciprocal reaction of the alkaline salts of alkylcarbonic acid with chlorocarbonic esters, is described.

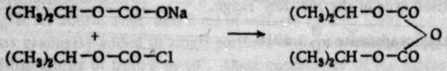
We previously used this method for the synthesis of dimethyl- and diethylpyrocarbonates, and also of certain mixed esters of pyrocarbonic acid, and it gave excellent results under these conditions [1, 2].

The starting materials for the synthesis of diisopropylpyrocarbonate consisted of the sodium salt of isopropylcarbonic acid and the isopropyl ester of chlorocarbonic acid.

The sodium salt of isopropylcarbonic acid was prepared by Beilstein's method [3], and the isopropyl ester of chlorocarbonic acid was prepared by Dumas' method [4].

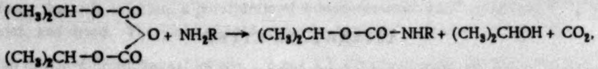
The diisopropylpyrocarbonate which we obtained consisted of a colorless liquid, with a rather pleasant, characteristic odor, which was insoluble in water but quite soluble in ether, alcohol, benzene and other organic solvents.

The structure of this compound as an ester of pyrocarbonic acid and at the same time, as an anhydride of isopropylcarbonic acid, was determined above all by its synthesis, which is expressed by the following equation:



$$\begin{matrix}(CH_3)_2CH-O-CO-ONa\\+\\(CH_3)_2CH-O-CO-Cl\end{matrix}\longrightarrow\begin{matrix}(CH_3)_2CH-O-CO\\ \\(CH_3)_2CH-O-CO\end{matrix}\!>O$$

In addition, the structure of the ester was demonstrated by its reactions with ammonia and aniline, which proceeded entirely analogously to the reactions of diethylpyrocarbonate with the same reagents and led to the formation, respectively, of the isopropyl ester of carbamic acid and the isopropyl ester of phenylcarbamic acid



$$\begin{matrix}(CH_3)_2CH-O-CO\\ \\(CH_3)_2CH-O-CO\end{matrix}\!>O+NH_2R\longrightarrow(CH_3)_2CH-O-CO-NHR+(CH_3)_2CHOH+CO_2,$$

where R = H and C_6H_5.

The structure of the compound obtained was confirmed by its molecular refraction, which coincided with that calculated for diisopropylpyrocarbonate.

EXPERIMENTAL

1. Preparation of Diisopropylpyrocarbonate. Starting materials: a) 18 g (about 0.14 mole) of the sodium salt of isopropylcarbonic acid; sodium content 18.42%, calculated sodium content for $C_4H_7O_3Na$, 18.24%;

b) 52.5 g (about 0.43 mole) of the isopropyl ester of chlorocarbonic acid with a b.p. of 103-105°; b.p. 103° [5] according to the literature data.

The mixture of the well-ground sodium salt of isopropylcarbonic acid and the isopropyl ester of chlorocarbonic acid was placed in a round-bottomed flask, 100-150 ml in capacity, equipped with a reflux condenser with a calcium chloride tube and a mechanical stirrer with a mercury seal. The reaction mixture was heated for 7 hours on a water bath at 60-65°, with constant energetic stirring. On the following day, the mixture was drawn off on a Büchner funnel and the precipitate on the funnel was washed with a small quantity of dry ethyl ether. After the ether and the unreacted chlorocarbonic ester had been distilled off, the residue was fractionated in a vacuum. 13.5 g distilled over at 6 mm in the 88-88.5° range. The yield was 50%.

d_4^{20} 1.0374; n_D^{20} 1.4015; MR_D 44.46; calculated 44.10.

0.2618 g sub.: 0.4840 g CO_2; 0.1764 g H_2O. 0.1996 g sub.: 15.18 g benzene: Δt 0.355°. Found %: C 50.42; H 7.53. M 191.03. $C_8H_{14}O_5$. Calculated %: C 50.52; H 7.42. M 190.19.

2. Isopropyl ester of carbamic acid. A saturated solution of ammonia in ethyl alcohol was added to 1 g of diisopropylpyrocarbonate. The reaction began quickly and proceeded rather energetically: evolution of heat in the liquid and formation of carbon dioxide gas (barium hydroxide solution) were observed. After evaporating off the alcohol and drying in a vacuum desiccator over calcium chloride, we obtained colorless crystals with a m.p. of 93-94°; according to the literature data for the isopropyl ester of carbamic acid, the m.p. is 92-93° [5]. The yield was 0.53 g (98%).

0.2316 g sub.: 20.8 ml H_2SO_4 (0.10644 N). Found %: N 13.38. $C_4H_9O_2N$. Calculated %: N 13.56.

3. Isopropyl ester of phenylcarbamic acid. 1.9 g of diisopropylpyrocarbonate was added in the form of drops to 0.9 g of freshly distilled aniline. Evolution of heat in the mixture and of carbon dioxide gas determined with barium hydroxide solution was observed. The contents of the test tube were converted by cooling into a solid crystalline mass. After recrystallization from alcohol, it consisted of long needles with a m.p. of 86-87°; according to the literature data for the isopropyl ester of phenylcarbamic acid, the m.p. is 90° [6], 75-76° [7], 42-43° [8]. The yield was 1.74 g (97%).

0.4756 g sub.: 24.6 ml H_2SO_4 (0.10644 N). Found %: N 7.71. $C_{10}H_{13}O_2N$. Calculated %: N 7.81.

4. Pyrolysis of diisopropylpyrocarbonate. About 4 g of diisopropylpyrocarbonate was heated in a small flask with a reflux condenser on a sulfuric acid bath with a thermometer which was immersed in the liquid under investigation. At a temperature of 183°, an insignificant evolution of fine bubbles of gas was noted. The temperature rather rapidly rose to 196-200°, after which it did not change for at least 20 minutes.

After this, the reflux condenser was replaced with a straight condenser and the liquid was distilled off from the flask; the entire liquid distilled over in the 196-200° range.

n_D^{20} 1.4016; for diisopropylpyrocarbonate n_D^{20} 1.4015.

SUMMARY

1. Diisopropylpyrocarbonate, which was unknown in the literature, has been synthesized.

2. A new reaction for preparing the isopropyl esters of carbamic and phenylcarbamic acids with almost quantitative yields was described.

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* See Consultants Bureau Translation, page.

QUESTION OF PREPARING BROMINE-SUBSTITUTED BENZALDEHYDE DERIVATIVES

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To prepare aromatic aldehydes, the method of oxidizing the corresponding methyl-substituted benzene is widely used; manganese dioxide or chromic anhydride is usually used as the oxidizing agent but selenious anhydride has recently been recommended for this. However, for the preparation of a number of bromine-substituted benzaldehydes, and specifically 3-bromobenzaldehyde and 3,5-dibromobenzaldehyde, not the route of oxidizing the corresponding bromo-substituted toluenes, but rather other, more complex, synthetic methods are recommended in the literature.

Since it was necessary for us to conduct investigations among the bromine derivatives of benzaldehyde indicated above, we decided to investigate the possibility of synthesizing them by oxidizing the corresponding bromine-substituted toluenes, the preparation of which presented no great difficulties. We used chromic anhydride as the oxidizing agent. The experiments which were performed proved that it is entirely possible to use the oxidation method to prepare the bromine-substituted benzaldehydes indicated above.

EXPERIMENTAL

Preparation of 3-bromobenzaldehyde. 6.3 g of 3-bromotoluene was dissolved in a mixture of 40 ml of acetic anhydride, 30 ml of glacial acetic acid, and 6 ml of sulfuric acid (d 1.83), and cooled to 0°, after which 10 g of chromic anhydride was gradually added in small portions while the mixture was being energetically stirred and the temperature kept within limits of from 0 to 10°. Upon completion of the oxidation, the thick mass was poured onto ice and the pasty white precipitate was separated, washed with water and heated with 50 ml of 20% sulfuric acid for 1 hour. After cooling, the acidic solution was neutralized with soda and the 3-bromobenzaldehyde was extracted with ether. After drying over roasted sodium sulfate, the ether was first distilled off and then the oil which was left was distilled off. The yield of 3-bromobenzaldehyde with a b.p. of 233-236° amounted to 2 g (30%).

On acidifying the soda solution, a precipitate of 3-bromobenzoic acid was obtained, which was separated, washed with water, and dried. The yield of acid with a m.p. of 154° amounted to 2 g (27%).

Preparation of 3,5-dibromobenzaldehyde. 2 g of 3,5-dibromotoluene was dissolved in a mixture of 20 ml of acetic anhydride, 15 ml of glacial acetic acid and 3 ml of sulfuric acid (d 1.83), after which the mixture was cooled to 0° and 3 g of finely ground chromic anhydride was added, while the mixture was being energetically stirred mechanically, over a period of 2.5 hours; this procedure was followed to keep the temperature of the reaction mixture in the 0-10° range. Upon completion of the oxidation, the thick reaction mass was poured onto ice and the precipitate was separated, washed with water and heated for 1 hour on metal gauze with 30 ml of 20% sulfuric acid. After cooling, the precipitate was separated, washed with water, with soda solution, and again with water. The yield of 3,5-dibromobenzaldehyde amounted to 1.3 g (62%). The m.p. was 85-90°, which was in accord with the literature data.

An attempt to prepare 4-bromobenzaldehyde by oxidizing 4-bromotoluene with selenium dioxide in a sealed tube for 4 hours at 225-230° ended in failure; the yield of aldehyde did not exceed 11%. It was also of interest to note that the oxidation of 2,4,6-tribromotoluene did not lead to a postivie result; under the conditions indicated above, it was not oxidized either by chromic or by selenious anhydride and could be almost quantitatively recovered from the reaction mixture. This result can be explained by the presence of steric hindrance.

SUMMARY

The possibility of preparing certain bromine derivatives of benzaldehyde by the oxidation of the corresponding bromine-substituted toluenes with the aid of chromic and selenious anhydrides was investigated. The possibility of the preparative synthesis of 3-bromobenzaldehyde and 3,5-dibromobenzaldehyde was shown. The difficult oxidizability of 4-bromotoluene and the unoxidizability of 2,4,6-tribromotoluene under the given conditions, which can be explained by the presence of steric hindrance, were established.

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ACTION OF DIMETHYLACETYLENYLCARBINOLMAGNESIUM BROMIDE ON o-SALICYLALDEHYDE

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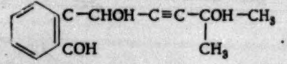
The preparation of unsaturated hydroxy compounds by the action of acetylenylcarbinolmagnesium bromides on aldehydes has been little studied. Syntheses based on acetylene and vinylacetylene [1] merit attention in this field.

In the present work, we have set ourselves the task of studying the action of dimethylacetylenylcarbinolmagnesium bromides on o-salicylaldehyde. The investigations showed that, under specific conditions, it is possible to obtain the normal reaction product — an unsaturated phenolglycol. The indicated compound was obtained in the form of an oil which crystallized in 15-20 days and more rapidly upon addition of benzene or toluene. The crystals melted at 97-99°. Upon heating to 100°, they became rose colored; at 110-120°, dark violet colored; and in the 150° range, brown.

In the course of 3-4 months in air, these crystals gradually change color from bright rose to violet. The colored substance is readily soluble in ether, and after evaporating off the ether, a dark violet lac, which is insoluble in water and rather stable to heating, is left.

Thus, as a result of the reaction, 1-o-hydroxyphenyl-4-methylpentyne-2-diol-1,4 was obtained:



It is entirely possible that the violet colored substance consists of a product of its isomeric conversion.

EXPERIMENTAL

45 g of dimethylacetylenylcarbinol, dissolved in an equal volume of dry ether, was added in the form of drops to ethyl magnesium bromide formed in the usual way (24.5 g of magnesium and 130 g of ethyl bromide). After addition of the carbinol, the stirring was continued for 3-4 hours more. 30 g of o-salicylaldehyde, dissolved in 30 ml of ether, was added to the mixture while it was being cooled with ice and being stirred. After addition of the aldehyde, the reaction mixture was heated for 10-15 minutes at 40°. The mixture was left for 24 hours and was then decomposed with 15% ammonium sulfate and then with 25-30% sulfuric acid.

The ethereal solution was dried with sodium sulfate. After distilling off the ether, a yellowish oil was left, which decomposed upon distillation (2 mm). Upon addition to the oil of an insignificant quantity of benzene or toluene, crystals with a m.p. of 97-99° (from benzene) precipitated. The crystals were quite soluble in ether and acetone, comparatively difficultly soluble in benzene and toluene, and insoluble in water. The yield was 13.5 g (26.6%).

0.1020 g sub.: 2602 g CO_2: 0.0570 g H_2O. 0.0107 g sub.: 0.11 g camphor: Δt 19°. 0.0450 g sub.: 15.7 ml CH_4 (17°, 727 mm). Found %: C 69.56; H 6.31; M 203.2. $C_{12}H_{11}(OH)_3$. Calculated %: C 69.90; H 6.70; M 206; 16.3 ml CH_4.

SUMMARY

1. The phenol alcohol, 1-o-hydroxyphenyl-4-methylpentyne-2-diol-1,4 was synthesized for the first time by the action of dimethylacetylenylcarbinolmagnesium bromide on o-salicylaldehyde.

2. Upon heating the indicated compound to 100°, it became rose-colored; upon further increase in temperature, it became violet, and then brown. Such color changes were also observed upon keeping the crystals for 3-4 months.

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SYNTHESIS OF PYRIMIDINOIMIDAZOLONES

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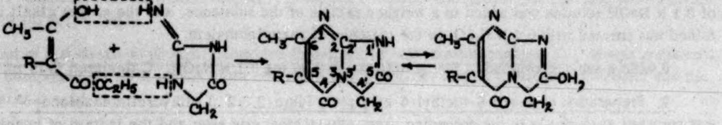
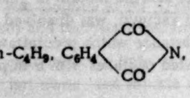
As we have previously demonstrated, pyrimidinoimidazolones can be prepared by closing the imidazolone ring as a result of the action of ammonia on bromoacyl derivatives of 2-aminopyrimidines, and also by the condensation of acetoacetic ester with α-guanidoaliphatic acids [1].

In the present work, we attempted to prepare pyrimidino-2,3:2',3'-dihydroimidazolones starting from the lactam of guanidoacetic acid and certain derivatives of acetoacetic and malonic ethers. This condensation readily leads to the formation of pyrimidine systems analogously to what occurs in the reaction of 2-aminoimidazole or imidazoline derivatives with acetoacetic ester and with other compounds similar to it [2].

The reaction between the lactam of guanidoacetic acid and alkyl derivatives of acetoacetic ester proceeds according to the scheme:



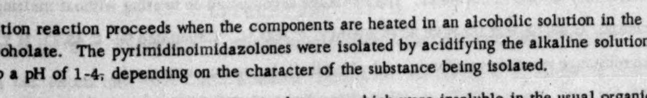
where R = H, C_2H_5, n-C_4H_9,



$C_6H_4\langle{}^{CO}_{CO}\rangle N$,

giving 4-oxo-5-alkylpyrimidino-2,3:2',3',-dihydroimidazolone-5'.

The condensation of the lactam of guanidoacetic acid with malonic ester and its derivatives, which leads to the formation of the corresponding 4,6-dioxopyrimidino-2,3:2',3'-dihydroimidazolone-5' compounds, proceeds analogously:



where R = CH_3, C_2H_5.

The condensation reaction proceeds when the components are heated in an alcoholic solution in the presence of sodium alcoholate. The pyrimidinoimidazolones were isolated by acidifying the alkaline solution with hydrochloric acid to a pH of 1-4, depending on the character of the substance being isolated.

The compounds prepared consisted of crystalline substances which were insoluble in the usual organic solvents, difficultly soluble in hot water, and comparatively readily soluble in dilute alkalis.

The pyrimidinoimidazolones synthesized have high melting points, or are decomposed by heating and do not melt.

The compounds obtained are capable of forming salts with alkalis. The 4-oxo-5-alkyl-pyrimidino-2,3:2',3'-dihydroimidazolone-5' compounds have 1 acidic hydrogen atom, which apparently arises due to lactam-lactim tautomerism.

The acidity of the compound increases with increasing number of oxogroups in the pyrimidine ring. Thus, 4,6-dioxopyrimidino-2,3:2',3'-dihydroimidazolone-5' requires about 2 moles of alkali for neutralization.

EXPERIMENTAL

1. Preparation of 4-oxo-5,6-dimethylpyrimidino-2,3:2',3'-dihydroimidazolone-5'. 1 g of the lactam of guanidoacetic acid, obtained by the dehydration of guanidoacetic acid [3] was added to an alcoholic solution of sodium ethylate (prepared from 0.92 g of metallic sodium and 50 ml of anhydrous ethyl alcohol) in a three-necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser and protected with a $CaCl_2$ tube. The resultant solution was heated to boiling, 7.2 g of methylacetoacetic ester was introduced into it, and the reaction mixture was boiled for 5 hours.

The alcohol and the methylacetoacetic ester which had not reacted were then distilled off in vacuum, and 5% hydrochloric acid was added to the residue in such a quantity that the solution had a pH of 1.

The precipitate which settled out was filtered off, washed with ether, and recrystallized from 60 parts of water. The yield was 50.3%. The substance consisted of a light crystalline powder with a m.p. of 289-290° (with decomposition). It was soluble in hot water, poorly soluble in cold water, and insoluble in the usual organic solvents.

Found %: C 53.93; H 5.11; N 23.44 (Kjeldahl). $C_8H_9O_2N_3$. Calculated %: C 53.63; H 5.03; N 23.46.

The substance reacted as a monobasic acid with alkali.

The determination was carried out in the following manner. An excess (relative to the calculated quantity) of 0.1 N NaOH solution was added to a weighed sample of the substance, and the excess alkali in the solution obtained was titrated with 0.1 N H_2SO_4 in the presence of phenolphthalein.

0.0486 g sub.: consumed in the neutralization 2.86 ml 0.1 N NaOH. Calculated 2.70 ml 0.1 N NaOH.

2. Preparation of 4-oxo-6-methyl-5-ethylpyrimidino-2,3:2',3'-dihydroimidazolone-5'. The substance was prepared analogously to the preceding, from ethylacetoacetic ester and the lactam of guanidoacetic acid. The dry residue obtained after concentrating the reaction mixture in a vacuum, was dissolved in 5% hydrochloric acid, and the solution which was formed was brought to pH 2. The substance which precipitated was filtered off, washed with ether, and recrystallized from 80 parts of water. It consisted of flakes with a m.p. of 261-262° (with decomposition). The yield was 27%.

The substance was insoluble in cold water and in organic solvents, and was soluble in hot water and in dilute alkalis.

Found %: N 21.74, 21.79 (Kjeldahl). $C_9H_{11}O_2N_3$. Calculated %: N 21.76.

The substance reacted as a monobasic acid with alkali.

0.0589 g sub.: consumed in the neutralization 3.11 ml 0.1 N KOH. Calculated 3.03 ml 0.1 N KOH.

3. Preparation of 4,6-dioxopyrimidino-2,3:2',3'-dihydroimidazolone-5'. It was prepared analogously to the preceding, from malonic ester and the lactam of guanidoacetic acid.

To isolate the product formed, the dry residue left after concentrating the reaction mixture in a vacuum was treated with such a quantity of 5% hydrochloric acid that the solution formed had a pH of 4. The substance which precipitated was filtered off, washed with ether, and recrystallized from 70 parts of boiling water. The yield was 66.7%. The preparation consisted of a yellowish powder which was insoluble in organic solvents and in cold water, and was difficultly soluble in hot water. The substance decomposed on heating without melting.

Found %: C 43.13; H 3.16; N 25.03 (Kjeldahl). $C_6H_5O_3N_3$. Calculated %: C 43.11; H 2.99; N 25.14.

The substance reacted as a dibasic acid with alkali, but not quantitatively.

0.0510 g sub.: consumed in the neutralization 5.12 ml 0.1 N NaOH. Calculated (for reaction with 2 moles of NaOH) 6.00 ml 0.1 N NaOH.

4. Preparation of 4,6-dioxo-5-ethylpyrimidino-2,3:2',3'-dihydroimidazolone-5'. It was prepared analogously to the preceding, from the diethyl ester of ethyl malonic acid and the lactam of guanidoacetic acid.

The dry residue, obtained after concentrating the reaction mixture in a vacuum, was dissolved in 5% hydrochloric acid, and the solution which was formed was brought to pH of 1.

The substance which settled out in the precipitate was filtered off, washed with ether, and recrystallized from 25 parts of water. It consisted of coarse flakes with a m.p. of 292-293° (with decomposition). The yield was 51%.

The substance was insoluble in cold water and organic solvents, and soluble in hot water and in dilute alkalis.

Found %: N 21.55, 21.71 (Kjeldahl). $C_8H_9O_3N_3$. Calculated %: N 21.53.

Reaction of the substance with alkali:

0.0640 g sub.: consumed in the neutralization 4.05 ml 0.1 N KOH. Calculated (for reaction with 2 moles of KOH) 6.42 ml 0.1 N KOH.

5. Preparation of 4,6-dioxo-5-butylpyrimidino-2,3:2',3'-dihydroimidazolone-5'. It was prepared analogously to the compound described above, from the diethyl ester of butylmalonic acid and the lactam of guanidoacetic acid.

The substance was isolated at pH 2. It was recrystallized from 120 parts of boiling water. The yield was 71.7%.

The preparation was insoluble in cold water and in organic solvents, difficultly soluble in hot water, and soluble in dilute alkalis. The m.p. was 278° (with decomposition).

Found %: C 54.10; H 5.89; N 19.01 (Kjeldahl). $C_{10}H_{13}O_3N_3$. Calculated %: C 53.81; H 5.83; N 18.83.

Reaction of the substance with alkali:

0.0525 g sub.: consumed in the neutralization 3.50 ml 0.1 N NaOH. Calculated (for reaction with 2 moles of NaOH) 4.50 ml 0.1 N NaOH.

6. Preparation of 4,6-dioxo-5-phthalimidopyrimidino-2,3:2',3'-dihydroimidazolone-5'. It was prepared analogously to the compound set forth above, from equimolecular quantities of phthalimidomalonic ester and the lactam of guanidoacetic acid.

The substance was isolated at pH 2, carefully washed with ether (to separate the phthalimidomalonic ester which had not reacted) and recrystallized from 48 parts of 85% formic acid. The yield was 20.5%.

The substance consisted of a light yellowish powder which was insoluble in cold water and in organic solvents, difficultly soluble in hot water, and soluble in formic acid and dilute alkalis. The substance decomposed on heating without melting.

Found %: C 53.72; H 2.62; N 18.15 (Kjeldahl). $C_{14}H_8O_5N_4$. Calculated %: C 53.85; H 2.56; N 17.95.

Reaction of the substance with alkali:

0.0544 g sub.: consumed in the neutralization, 4.70 ml of 0.1 N NaOH. Calculated (for reaction with 3 moles of NaOH) 5.25 ml 0.1 N NaOH.

SUMMARY

1. It was shown that the lactam of guanidoacetic acid can condense with compounds of the acetoacetic and malonic ester type to give the corresponding pyrimidino-2,3:2',3'-dihydroimidazolone-5' compounds.

2. It was established that the pyrimidino-2,3:2',3'-dihydroimidazolone compounds obtained have acidic properties; the acidity of the compounds increases with increasing number of oxo-groups in the pyrimidine ring.

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INVESTIGATIONS IN THE FIELD OF QUINONES

I. SULFONATION OF QUINONES

A. P. Terentyev and A. N. Grinev

A. A. Voskresensky [1], who prepared p-benzoquinone for the first time, reported in the course of studying its properties that this compound is carbonized by the action of concentrated sulfuric acid and that a flocculent brown precipitate is obtained with less concentrated sulfuric acid. As was subsequently established by Liebermann [2], the precipitate consists of a polymer of p-benzoquinone which contains a small quantity of the trimer [3]. Dark resinification products are also obtained by the action of fuming sulfuric acid [4] and chlorosulfonic acid [5] on p-benzoquinone. We observed a similar phenomenon upon treating quinone with a solution of sulfuric anhydride in dichloroethane. Toluquinone is very readily polymerized by both concentrated sulfuric acid [6] and dilute sulfuric acid [3, 6]. Other substituted quinones – p-xyloquinone, α-naphthoquinone – do not react with strong sulfuric acid at ordinary temperatures [7, 8], but are decomposed on heating [8, 9]. β-Naphthoquinone [10] and duroquinone [11] behave analogously.

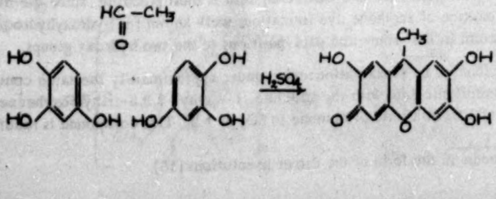
Experiments involving the sulfonation of quinones which did not lead to positive results [2, 4, 5, 12] are described in the literature. The fundamental cause of this failure lies in the fact that for sulfonating the quinones, agents were used which were capable not only of sulfonating, but also of causing polymerization of the quinones; the latter reaction proceeds at a greater rate than the sulfonation. In our preliminary communication [13], we indicated that if the sulfonation is conducted under conditions which exclude polymerization (absence of hydrogen ions) and oxidation, the sulfonic acids can be obtained in the form of the salts with quite satisfactory yields.

We used dioxansulfotrioxide (the complex of sulfuric anhydride with dioxan) as the sulfonating agent. The reaction was conducted in the complete absence of moisture, while the subsequent treatment was performed in a carbon dioxide atmosphere. Before treatment with barium carbonate, it was necessary to eliminate the quinone which had not reacted, since the latter reacts with the carbonates of the alkali and alkaline earth metals to form unstable colored compounds.

p-Benzoquinone. Hydroxyhydroquinonesulfonic acid, in the form of the barium salt, was isolated as the chief sulfonation product in a yield of 56% with a molecular ratio of quinone to sulfuric anhydride of 1:3 at ordinary temperature. This compound had not previously been described in the literature.

The analytical data and properties confirmed the structure of this compound. The barium and sodium salts are stable in the dry state; upon moistening with water, energetic oxidation begins: initially the salt quickly darkens (partial conversion into the quinone with formation of colored quinhydrones), and then the salt becomes light cream-colored. Upon more prolonged oxidation, the formation of a resinified product occurs. Weak aqueous solutions of the salt of hydroxyhydroquinonesulfonic acid give a cherry-red color with ferric chloride or quinone solutions.

Cleavage of the sulfuric acid is not observed upon boiling with dilute acids, which indicates that the sulfo group is located on a carbon and not on an oxygen atom. The presence of three hydroxyl groups was demonstrated by methylation, a trimethoxy compound being formed [14]. A characteristic reaction for hydroxyhydroquinone appears to be the formation of a xanthene dye [15] as a result of the action of acetaldehyde in the presence of sulfuric acid according to the scheme:

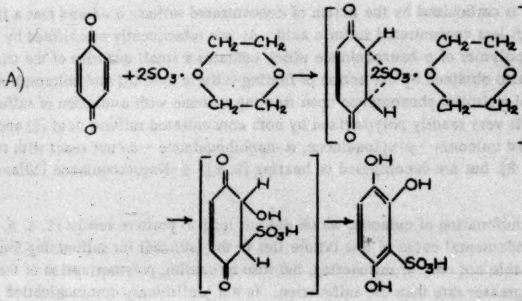


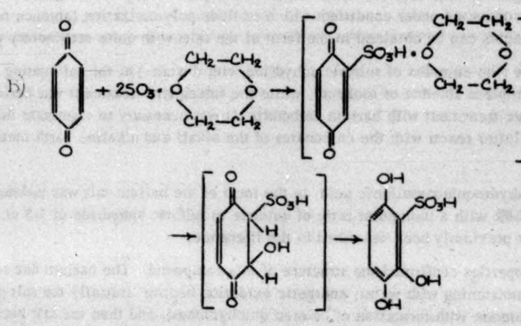
In fact, an intense brick-red color is obtained by heating a sample of the potassium salt of the sulfonic acid with paraldehyde and sulfuric acid.

The infra-red absorption spectrum of the barium salt in aqueous solution showed the presence of the 1038 and 992 cm^{-1} frequencies which are characteristic of the benzene structure.

Thus, the sulfonation of p-benzoquinone can be represented by Scheme A.*

It might be assumed that the first reaction product would be the dioxan salt of the sulfonic acid, which, in the treatment process, would add the elements of water and upon isomerizing, would yield the hydroxyhydroquinonesulfonic acid (Scheme B).





However, this is improbable. The presence of hydrogen ions in the dioxan solutions causes a strong resinification of quinone; as a result of the action of even a 10% solution of sulfuric acid in dioxan or a dioxan solution of toluenesulfonic acid, profound resinification of p-benzoquinone occurs. Thus, it must be assumed that the reaction proceeds in accordance with the first scheme.

The disulfohydroxyhydroquinone (1,2,4-trihydroxybenzenedisulfonic-3,5 acid) is obtained by the sulfonation of p-benzoquinone with a considerable excess of dioxansulfotrioxide (6 moles per 1 mole of quinone). [See top of following page.]

This structure for hydroxyhydroquinone-disulfonic acid is most probable, since the disulfonic acid does not give the characteristic reaction of xanthene dye formation, well-known for hydroxyhydroquinone and its derivatives which have a hydrogen atom in the ortho- and para-positions to the two hydroxy groups.

Toluquinone is sulfonated by dioxansulfotrioxide under approximately the same conditions as apply to p-benzoquinone. The monosulfonic acid with the structure, 1-methyl-2,3,5-trihydroxybenzenesulfonic-4 acid (I), was obtained in a yield of 53% at a ratio of quinone to SO_3 of 1:2. This compound is readily oxidized, similarly

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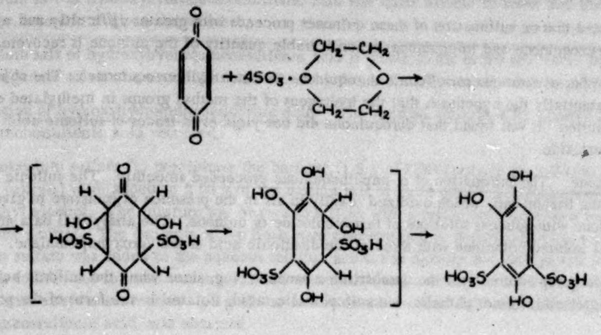
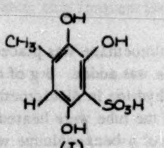
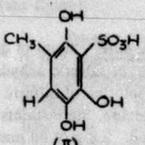
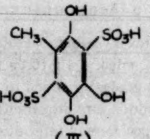
* Dioxansulfotrioxide occurs in the form of the dimer in solutions [16].



to hydroxyhydroquinonesulfonic acid, and gives a color reaction as a result of the action of quinone solution and ferric chloride. The sulfonic acid condenses with paraldehyde in alcoholic solutions of sulfuric acid to give the typical reaction of xanthene dye formation. The latter reaction also permits the presence of the sulfo group in the para-position to the methyl group to be verified, since only in this case would there be a hydrogen atom in the ortho-para positions to two hydroxy groups in the compound, and not the other isomer (II).

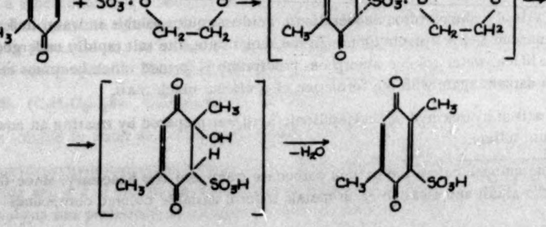

(I)


(II)


(III)

At a considerable excess of the sulfonating agent, the chief reaction product obtained is the disulfonic acid having, evidently, structure (III) (1-methyl-2,4,5-trihydroxybenzenedisulfonic-3,6 acid). This compound does not give a color reaction with paraldehyde.

p-Xyloquinone and m-xyloquinone yield, as a result of the action of dioxansulfotrioxide, monosulfonic acids of the quinoid type (1,4-dimethylcyclohexadiene-1,4-dione-3,6-sulfonic-2 acid and 1,3-dimethylcyclohexadiene-3,6-dione-2,5-sulfonic-4 acid). The barium salts of the sulfonic acids, obtained by treatment of the sulfonated mass, do not darken in the air and do not give a color reaction with quinone solution, while, on the other hand, they do form colored solutions when hydroquinone is added. It is evident that the dioxansulfotrioxide addition product when treated with water, is incapable of isomerizing into hydroxyhydroquinone, and eliminates the elements of water to give the sulfoquinone:



The disulfonic acid (1,4-dimethylcyclohexadiene-1,4-dione-3,6-disulfonic-2,5 acid) is obtained as the chief product of the action of a considerable excess of sulfonating agent on p-xyloquinone.

It should be noted that the sulfonation of these quinones proceeds with greater difficultly and with smaller yields than with p-benzoquinone and toluquinone; a considerable quantity of the quinone is recovered.

We made a number of attempts to sulfonate duroquinone (tetramethylbenzoquinone). The object of the work was to verify circumstantially the hypothesis that the hydrogens of the methyl groups in methylated quinones can participate in the reaction. It was found that duroquinone did not yield even traces of sulfonic acids with a great excess of dioxansulfotrioxide.

α-Naphthoquinone. The sulfonation of α-naphthoquinone proceeded smoothly. The sulfonic acid was isolated in the form of the barium salt, which oxidized readily in air in the presence of moisture to give the cherry-red color of quinhydrone with aqueous solutions of ferric chloride or quinone. The analytical data and properties of the salt which was isolated coincided with those of the disulfonic acid of trihydroxynaphthalene.

The second sulfo group entered into the unsubstituted benzene ring, since when the sulfonic acid salt was oxidized by Miller's method [17], not phthalic, but sulfophthalic, acid, isolated in the form of the potassium salt, was obtained.

β-Naphthoquinone. The sulfonation of β-naphthoquinone was conducted at a temperature of 0 to 10°; under these conditions the quinone was partially polymerized. The analytical data and the properties of the sulfonic acid, isolated in the form of the barium salt, agreed with those of the disulfonic acid of β-naphthoquinone. The salt did not give a coloration with ferric chloride and was stable to oxidation by atmospheric oxygen.

EXPERIMENTAL

1. Sulfonation of p-Benzoquinone

Preparation of hydroxyhydroquinonesulfonic acid. 30 ml of dichloroethane was placed in a sealing tube and, then, while it was being cooled, 5.4 g (0.09 mole) of sulfuric anhydride was added. 6 g of dioxan (a small excess over the theoretical) was gradually added to the solution of sulfuric anhydride in dichloroethane. In order to convert all the sulfuric anhydride into dioxansulfotrioxide, the contents of the tube were heated for a short time. The precipitate which thereupon formed later dissolved. 2.8 g (0.03 mole) of p-benzoquinone with a m.p. of 116° was added to the cooled solution of dioxansulfotrioxide. The tube was sealed and shaken for 25-30 hours at room temperature. The reaction had to be conducted in the complete absence of moisture, since otherwise, polymerization of the quinone, caused by the presence of hydrogen ions, occurs.

After the tube was opened, its contents were poured into 400-500 ml of water which was being stirred with a mechanical stirrer. The yellow solution which formed was concentrated in a vacuum at 40-50° in a carbon dioxide atmosphere to half its initial volume; at the same time, the unreacted quinone* was steam distilled off. The solution, while being vigorously stirred, was poured into an aqueous suspension of barium carbonate. The precipitate was separated. The completely transparent solution of the barium salt of hydroxyhydroquinonesulfonic acid was concentrated to dryness at 50-60° in a carbon dioxide atmosphere. After the concentration, a crystalline white precipitate of the barium salt of hydroxyhydroquinonesulfonic acid formed in the flask.

The salt was precipitated from methyl alcohol by the addition of 100-150 ml of ether in the form of fluffy white crystals which were quickly separated and, after abundant washing with anhydrous ether, were dried in a vacuum desiccator over calcium chloride. The barium salt of hydroxyhydroquinonesulfonic acid was stored in a vacuum desiccator over calcium chloride. The yield was 56%.

Found %: Ba 25.30. $(C_6H_5O_6S)_2Ba$. Calculated %: Ba 25.14.

The barium salt of hydroxyhydroquinonesulfonic acid was quite soluble in water and methyl alcohol, and insoluble in ether, benzene and petroleum ether. In the moist state, the salt rapidly undergoes change in air; under these conditions, a black, water-soluble amorphous precipitate is formed which becomes cream-colored on standing in air and then darkens again with the formation of a viscous black mass.

The sodium salt of hydroxyhydroquinonesulfonic acid was prepared by treating an aqueous solution of the barium salt with sodium sulfate.

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* Elimination of the quinone before the barium carbonate treatment was necessary, since the quinone reacts with the carbonates of the alkali and alkaline earth metals to form unstable colored compounds.

Found %: Na 10.26. $C_6H_5O_6SNa$. Calculated %: Na 10.08.

The sodium salt of hydroxyhydroquinonesulfonic acid was quite soluble in water and methyl alcohol, and insoluble in ether, benzene and petroleum ether.

The sodium salt of hydroxyhydroquinonesulfonic acid is stable in air in the dry state. Bromine water and potassium permanganate solution are rapidly decolorized by the action of aqueous solutions of the salt.

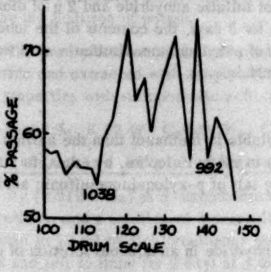
Methylation of hydroxyhydroquinonesulfonic acid. The method, described by Gentsch [14] for the methylation of pyrocatecholsulfonic acid was used.

3 g of potassium sulfate (to precipitate the barium), 1.5 g of KOH (ratio to the sulfonic acid, 3:1) and 8 g of methyl iodide (excess) were added to 2.08 g of the barium salt of hydroxyhydroquinonesulfonic acid dissolved in 200 ml of methyl alcohol. The mixture was heated in a flask with a reflux condenser on a water bath until the reaction became neutral. The contents of the flask were concentrated to dryness and extracted with hot water. 4.5 g of copper sulfate was added to the aqueous solution and sulfur dioxide was then passed into it. After separating the cuprous iodide, the solution was neutralized with potash and concentrated. The precipitate, after drying, was extracted with anhydrous alcohol. 0.3 g of the oxidation-stable potassium salt, which agreed in analysis with trimethoxybenzenesulfonic acid, was obtained.

Found %: K 13.89. $C_9H_{11}O_6K$. Calculated %: K 13.66.

The potassium salt of trimethoxybenzenesulfonic acid, consisted of white, hygroscopic crystals, quite soluble in water, poorly soluble in alcohol and insoluble in ether and benzene.

Spectrographic analysis of the barium salt of hydroxyhydroquinonesulfonic acid (the solvent was water), conducted with a Hilger spectrograph (sodium chloride prism) in the infra-red absorption spectrum, demonstrated the presence of the benzene ring frequencies* (see figure).



Preparation of hydroxyhydroquinonedisulfonic acid. 2.5 g (0.023 mole) of p-benzoquinone in 45 ml of dichloroethane with dioxansulfotrioxide, prepared from 11 g (0.137 mole) of sulfuric anhydride and 15 g of dioxan (excess), was placed in a sealing tube. The mixture was left at room temperature for 6 days. The reaction liquid was treated in exactly the same way as in the preparation of hydroxyhydroquinonesulfonic acid. The barium salt, which agreed in analysis and properties with the disulfonic acid of hydroxyhydroquinone, was prepared. The yield was 80%.

Found %: Ba 32.37. $C_6H_4O_9S_2Ba$. Calculated %: Ba 32.59.

The salt of hydroxyhydroquinonedisulfonic acid was quite soluble in water; the salt was 2-2.5 times less soluble in methyl alcohol than the barium salt of hydroxyhydroquinonesulfonic acid (2 g per 200 ml of methanol). Aqueous solutions of the salt gave a cherry-red color with aqueous solutions of quinone or ferric chloride.

The salt of the disulfonic acid did not give a xanthene dye on heating with paraldehyde and sulfuric acid.

2. Sulfonation of Toluquinone

Preparation of toluhydroxyhydroquinonesulfonic acid. 2 g (0.0165 mole) of dry and sublimed toluquinone (m.p. 69°) was added to a tube containing a solution of dioxansulfotrioxide prepared from 2 g (0.025 mole) of sulfuric anhydride and 3 g of dioxan in a solution of 20 ml of dichloroethane. After standing for 2 days, the contents of the tube were treated in the same way as in the sulfonation of p-benzoquinone. The barium salt of toluhydroxyhydroquinonesulfonic acid was prepared. The yield was 52%.

Found %: Ba 23.98. $(C_7H_7O_6S)_2Ba$. Calculated %: Ba 23.85.

The salt was quite soluble in water and moderately soluble in alcohol.

Preparation of toluhydroxyhydroquinonedisulfonic acid. The dioxansulfotrioxide prepared from 3 g (0.037 mole) of sulfuric anhydride and 4 g of dioxan was stirred into a solution of 1 g (0.008 mole) of toluquinone in

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* The spectrographic analysis was performed at our request by V. N. Vasilyeva.

10 ml of dichloroethane. The vessel was sealed and shaken for 60 hours. The reaction product was treated in the same way as the preceding. The yield was 67%.

Found %: Ba 31.48. $C_7H_6O_9S_2Ba$. Calculated %: Ba 31.54.

The barium salt of toluhydroxyhydroquinonedisulfonic acid was quite soluble in water and insoluble in ether, benzene and ligroin.

3. Sulfonation of p-Xyloquinone

p-Xyloquinone was prepared by oxidizing p-xylidine with potassium bichromate in a solution of 10% sulfuric acid [18]; the m.p. of 124.5-125° agreed with the literature data [18].

Preparation of p-xyloquinonesulfonic acid. 0.8 g (0.007 mole) of p-xyloquinone, dissolved in 6 ml of dichloroethane, was stirred into dioxansulfotrioxide prepared from 0.5 g (0.006 mole) of sulfuric anhydride and 1 g of dioxan in a sealing tube.

The transparent solution which formed was left for 2 days in a sealed tube at room temperature. The contents of the tube were then treated with 150-200 ml of water; under these conditions, a portion of the unreacted p-xyloquinone separated in the form of crystals. The aqueous solution was extracted with 50-70 ml of ether to eliminate the unreacted quinone, and, after elimination of the traces of ether, the aqueous layer was neutralized with barium carbonate. The filtrate was concentrated to dryness. The precipitate which formed was almost completely dissolved in methyl alcohol and was precipitated from the latter by ether. 0.4 g (24%) of the crystalline barium salt was obtained corresponding in its properties to the monosulfonic acid of p-xyloquinone.

Found %: Ba 24.33. $(C_8H_7O_5S)_2Ba$. Calculated %: Ba 24.18.

The salt was hygroscopic, did not darken in air and did not give a color with ferric chloride. Aqueous solutions of the salt had the red color of quinhydrone when hydroquinone was added to them. The salt was quite soluble in water; it was approximately 10 times less soluble in methyl alcohol than the barium salt of hydroxyhydroquinonesulfonic acid (0.2 g in 100 ml of methanol).

Preparation of the disulfonic acid of p-xyloquinone. 0.4 g (0.003 mole) of p-xyloquinone was added in a tube to a solution of dioxansulfotrioxide, prepared from 1 g (0.012 mole) of sulfuric anhydride and 2 g of dioxan dissolved in 10 ml of dichloroethane. After standing at room temperature for 3 days, the contents of the tube were treated in the same way as in the preceding experiment. The barium salt of p-xyloquinonedisulfonic acid was prepared and consisted of a white crystalline precipitate. The yield was 32%.

Found %: Ba 31.67. $C_8H_6O_8S_2Ba$. Calculated %: Ba 31.84.

The salt was quite soluble in water; it was somewhat more poorly soluble in methanol than the barium salt of p-xyloquinonesulfonic acid. The salt was precipitated from its solution in methyl alcohol, by ether, in the form of fluffy crystals. The salt was similar in its properties to the barium salt of p-xyloquinonesulfonic acid.

4. Sulfonation of m-Xyloquinone

m-Xyloquinone was prepared by oxidizing mesidine with chromic anhydride in an aqueous solution of dilute sulfuric acid [19]; the m.p. of 71.5-72° agreed with the literature data.

0.8 g (0.006 mole) of m-xyloquinone was stirred into 8 ml of dichloroethane with the dioxansulfotrioxide prepared from 1 g (0.012 mole) of sulfuric anhydride and 2.4 g of dioxan. The reaction was conducted in a sealed tube at room temperature for 3 days. The reaction product was treated in the same way as in the sulfonation of p-xyloquinone. The barium salt was prepared by precipitation from alcohol by ether in the form of white crystals with a yellowish tinge. The salt agreed in its analysis and properties with the monosulfonic acid of m-xyloquinone. The yield was 29%.

Found %: Ba 24.38. $(C_8H_7O_5S)_2Ba$. Calculated %: Ba 24.18.

The salt corresponded in its properties to the barium salt of p-xyloquinonesulfonic acid.

5. Sulfonation of Duroquinone

Dinitrodurene, obtained by the nitration of durene, served as the starting material for the preparation of the duroquinone. The dinitrodurene was reduced with stannous chloride to diaminodurene. The latter was isolated from the reaction mass by the addition of alkali and was extracted with ether. The ethereal extracts were washed with 15% hydrochloric acid. The diaminodurene hydrochloride, found in the aqueous layer, was oxidized into duroquinone by ferric chloride [20]. After recrystallization from alcohol, the duroquinone had a m.p. of 111°, which agreed with the literature data [21].

The sulfonation of duroquinone was conducted both under ordinary conditions and with heating (3 experiments). The reaction liquid was treated in the same way as in the preceding experiments. Barium was not detected in the water-soluble salts.

6. Sulfonation of α-Naphthoquinone

2 g (0.013 mole) of α-naphthoquinone with a m.p. of 125° was stirred in a tube with dioxansulfotrioxide (from 6 g of sulfuric anhydride and 8 g of dioxan) in a solution of 20 ml of dichloroethane. The tube was sealed and shaken for 30-40 hours at room temperature; then the contents of the tube were treated with 200 ml of water. The unreacted α-naphthoquinone was filtered off from the aqueous solution. The filtrate was treated in the same way as in the sulfonation of p-benzoquinone. The yield was 43%.

Found %: Ba 28.94. $C_{10}H_6O_9S_2Ba$. Calculated %: Ba 29.14.

The barium salt was quite soluble in water, soluble in methanol and insoluble in ether, benzene and ligroin. The precipitate of the barium salt readily underwent oxidation in air, with the formation of a black-colored amorphous mass.

Oxidation of the barium salt of the disulfonic acid [17]. The barium salt (1.5 g) was dissolved in 300 g of a 2% solution of sulfuric acid. The barium sulfate precipitate which formed was filtered off, and a 1% potassium permanganate solution was added from a buret to the filtrate while it was being stirred constantly; even after the addition of 100 ml of potassium permanganate, the solution was not decolorized. Further addition of the oxidizing agent (400 ml) was carried out with the solution heated to 80-90°. The attempt at oxidation was terminated when decolorization of the potassium permanganate did not occur even on heating. The manganese dioxide precipitate formed was filtered off, and the solution was concentrated on a water bath to small volume and extracted with ether. Phthalic acid was not detected in the ethereal layer after driving off the ether. Several drops of concentrated sulfuric acid were added to the aqueous layer, the solution was concentrated on a water bath to eliminate the volatile acids, and the thick liquid which was left was dissolved in 100 ml of water. The solution was neutralized with barium carbonate, the precipitate was filtered off, and the barium carbonate was precipitated from the filtrate by the addition of potash.

The precipitate which formed upon concentration of the filtrate was dried for a long time over phosphorus pentoxide and extracted with anhydrous alcohol. 0.3 g of a very hygroscopic potassium salt, which corresponded in its properties with sulfophthalic acid, was obtained.

Found %: K 32.49. $C_8H_3O_7SK_3$. Calculated %: K 32.54.

7. Sulfonation of β-Naphthoquinone

2 g (0.012 mole) of β-naphthoquinone (m.p. 115-117°, with decomposition) was dissolved in 25 ml of dichloroethane and a solution of dioxansulfotrioxide, prepared from 2 g (0.025 mole) of sulfuric anhydride and 4 g of dioxan in 20 ml of dichloroethane, was added to the orange solution of the β-naphthoquinone. The tube was sealed and left to stand for 2 days at a temperature of 0-10°. The contents of the tube were treated with 200 ml of water, the aqueous solution was neutralized with barium carbonate, and the solution of the barium salt was concentrated in a vacuum at a temperature of 40-60°.

The barium salt was reprecipitated from methyl alcohol with ether. The yield was 30%.

Found %: Ba 30.32. $C_{10}H_4O_8S_2Ba$. Calculated %: Ba 30.29.

The barium salt of the disulfonic acid of β-naphthoquinone did not give a color with ferric chloride. The salt decolorized bromine water and dilute potassium permanganate solution.

The barium salt of the disulfonic acid of β-naphthoquinone is hygroscopic, but stable to oxidation by atmospheric oxygen, and darkens only after prolonged standing in air.

SUMMARY

Typical quinones, which undergo profound resinification as a result of the action of the usual sulfonating agents, were successfully sulfonated with dioxansulfotrioxide. It was shown that, depending on the structure of the quinones and the conditions under which the reaction is conducted, the following results are obtained under these conditions: the sulfonation of p-benzoquinone leads to the formation of hydroxyhydroquinonesulfonic and hydroxyhydroquinonedisulfonic acids; of toluquinone, to methylhydroxyhydroquinonesulfonic, and methylhydroxyhydroquinonedisulfonic acids; of p-xyloquinone, to p-xyloquinonesulfonic, and p-xyloquinonedisulfonic acids; of m-xyloquinone, to m-xyloquinonesulfonic acid; of α-naphthoquinone, to trihydroxynaphthalenedisulfonic acid; and of β-naphthoquinone, to β-naphthoquinonedisulfonic acid.

The sulfonation proceeds via an intermediately-formed adduct of dioxansulfotrioxide, which is cleaved during the treatment, with formation of the indicated products.

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2-ALKOXYMETHYL- AND 2-ARYLOXYMETHYL-4(p-AMINOPHENYL)-THIAZOLES

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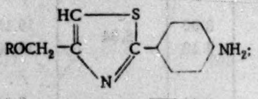
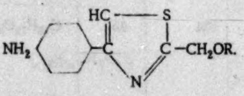
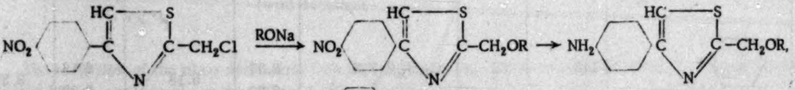
In a preceding work [1], the synthesis was described of 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles (A), prepared via the reaction of 4-chloromethyl-2-(p-nitrophenyl)-thiazole with alcohoblates and phenolates, with subsequent reduction of the nitro derivatives formed into the amino compounds.

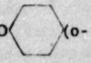
In the present article, the synthesis of thiazole derivatives (B), which differ from those previously described only in the position of the substituents in the thiazole ring, is described:


(A)

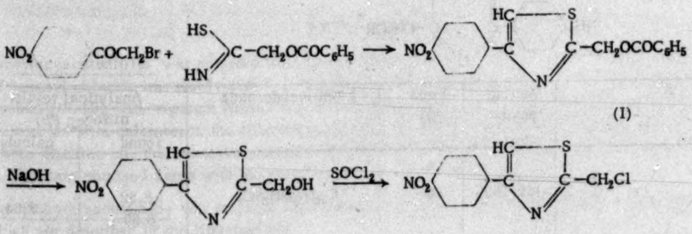

(B)

The synthesis of such compounds was accomplished via the reaction of 2-chloromethyl-4-(p-nitrophenyl)-thiazole with alcoholates and phenolates. The ethers of 2-hydroxymethyl-4-(p-nitrophenyl)-thiazole were then reduced into the corresponding amino derivatives according to the scheme:



where R = C_2H_5, n-C_4H_9, C_6H_5, p-C_6H_4Cl, CH_3O(o- and p-).

The initial 2-chloromethyl-4-(p-nitrophenyl)-thiazole was not known, and was prepared by us by nitrating 2-chloromethyl-4-phenylthiazole [2], also by condensing p-nitro-ω-bromoacetophenone with benzoyloxythioacetamide, saponifying the benzoyl derivative (I) which was formed into 2-hydroxymethyl-4-(p-nitrophenyl)-thiazole (II), and subsequently converting it into 2-chloromethyl-4-(p-nitrophenyl)-thiazole (III):


(I)

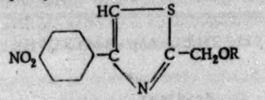
(II)

(III)

The 2-alkoxymethyl-4-(p-nitrophenyl)-thiazoles were prepared by heating 2-chloromethyl-4-(p-nitrophenyl)-thiazole with the corresponding alcoholates; the 2-aryloxymethyl-4-(p-nitrophenyl)-thiazoles were isolated in excellent yields by heating the 2-chloromethyl derivative with the corresponding phenols in acetone solution in the presence of anhydrous potash. The 2-alkoxymethyl- and 2-aryloxymethyl-4-(p-nitrophenyl)-thiazoles obtained are set forth in Table 1. All the preparations consisted of well-crystallized substances. The 2-alkoxymethyl-4-(p-nitrophenyl)-thiazoles were recrystallized from alcohol. The 2-aryloxymethyl derivatives were poorly soluble in alcohol; they were recrystallized from acetic acid.

TABLE 1

2-Alkoxymethyl-4-(p-nitrophenyl)-thiazoles of the General Formula:



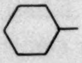
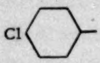
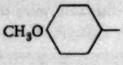
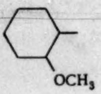
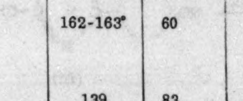
No.	R	Melting point	Yield (%)	Empirical formula	Analytical results			
					nitrogen (%)		sulfur (%)	
					found	calculated	found	calculated
IV	C_2H_5-	96-97°	78	$C_{12}H_{12}O_3N_2S$	10.40 10.43	10.60	12.13 11.97	12.12
V	n-C_4H_9-	60-61	77	$C_{14}H_{16}O_3N_2S$	9.67 9.72	9.58	11.23 11.00	10.98
VI		134	45	$C_{16}H_{12}O_3N_2S$	8.90 9.13	8.94	10.25 10.26	10.25
VII		160	62	$C_{16}H_{11}O_3N_2SCl$	7.78 7.93	8.08	8.86 8.92	9.23
VII		136-137	56	$C_{17}H_{14}O_4N_2S$	8.32 8.41	8.18	9.20 9.30	9.37
IX		113	62	$C_{17}H_{14}O_4N_2S$	8.07 8.20	8.18	9.18 9.29	9.37

TABLE 2

2-Aryloxymethyl-4-(p-aminophenyl)-thiazoles of the General Formula:



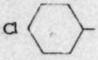
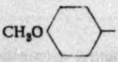
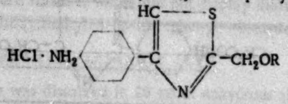
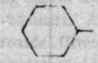
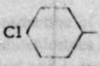
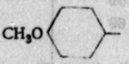
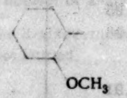
No.	R	Melting point	Yield (%)	Empirical formula	Analytical results	
					nitrogen (%)	
					found	calculated
X		162-163°	60	$C_{16}H_{13}ON_2SCl$	8.52 8.60	8.84
XI		139	83	$C_{17}H_{16}O_2N_2S$	9.23 9.26	8.97

TABLE 3

Hydrochlorides of 2-Alkoxymethyl- and 2-Aryloxymethyl-4-(p-aminophenyl)-thiazoles of the General Formula:



No.	R	Melting point	Empirical formula	Analytical results nitrogen (%)	
				found	calculated
XII	C_2H_5-	212-213°	$C_{12}H_{15}ON_2SCl$	10.52 10.61	10.35
XII		228-229	$C_{16}H_{15}ON_2SCl$	8.72 8.61	8.75
XIV		243	$C_{16}H_{14}ON_2SCl_2$	8.01 8.11	7.93
XV		222-224	$C_{17}H_{17}O_2N_2SCl$	7.92 7.78	8.03
XVI		183-184 (with decomp.)	$C_{17}H_{17}O_2N_2SCl \cdot HCl$	7.29 7.08	7.27

The reduction of the nitro derivatives into the corresponding amines was conducted in an alcoholic medium with iron filings, analogously to that of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles. Only two amines were isolated in the free form (Table 2); the others were identified in the form of the hydrochlorides and acetyl derivatives. The salts consisted of colorless needles and were purified by recrystallization from alcohol. The melting point and analytical data for the hydrochlorides obtained are set forth in Table 3. We did not succeed in obtaining the hydrochlorides of 2-butoxymethyl-4-(p-aminophenyl)-thiazole in analytically pure form.

The acetyl derivatives are set forth in Table 4; these derivatives were purified by recrystallization from acetic acid.

EXPERIMENTAL

Benzoyloxyacetonitrile was prepared from hydroxyacetonitrile and benzoyl chloride in the following manner. 1 mole of benzoyl chloride was slowly added, in the form of drops, to the reaction mixture, containing 1 mole of hydroxyacetonitrile [3], with vigorous stirring and at a temperature of 10-12°. The precipitate which settled out was then extracted with chloroform, the chloroform solution was dried with calcium chloride, and, after the solvent had been distilled off, the benzoyloxyacetonitrile was distilled in a vacuum at 143-145° (12 mm). The yield was 87%. The data obtained agree with the specifications in the literature [4].

Benzoyloxythioacetamide was prepared from benzoyloxyacetonitrile and hydrogen sulfide under the conditions which are described in the literature [4].

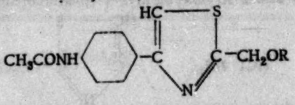
2-Chloromethyl-4-phenylthiazole was prepared from 2-hydroxymethyl-4-phenylthiazole and phosphorus oxychloride in accordance with the literature data [2].

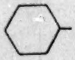
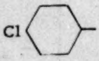
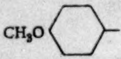
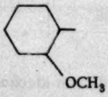
2-Benzoyloxymethyl-4-(p-nitrophenyl)-thiazole (I)

A mixture of 24.4 g of p-nitro-ω-bromoacetophenone and 21.4 g of benzoyloxythioacetamide in 25 ml of alcohol was carefully heated on a water bath until it began to boil, after which it was set aside from the bath and the reaction was allowed to continue to completion by itself (it was cooled when necessary). Upon completion of the boiling, the reaction mixture was heated for 15 minutes more on a boiling water bath and the yellow precipi-

TABLE 4

Acetyl Derivatives of 2-Alkoxymethyl- and 2-Aryloxymethyl-4-(p-aminophenyl)-thiazoles of the General Formula:



No.	R	Melting point	Empirical formula	Analytical results nitrogen (%) found	Analytical results nitrogen (%) calculated
XVII	C_2H_5-	149°	$C_{14}H_{16}O_2N_2S$	10.43 10.36	10.15
XVIII	n-C_4H_9-	147	$C_{16}H_{20}O_2N_2S$	9.35 9.50	9.21
XIX		174-175	$C_{18}H_{16}O_2N_2S$	8.49 8.49	8.64
XX		195	$C_{18}H_{15}O_2N_2SCl$	7.65 7.69	7.81
XXI		202	$C_{19}H_{18}O_3N_2S$	7.95 7.98	7.90
XXII		149	$C_{19}H_{18}O_3N_2S$	7.91 7.80	7.90

tate which formed was filtered off and dried in air. The weight of the crude product was 28.3 g (84%). The m.p. was 161°. After recrystallization from glacial acetic acid, the m.p. was 161°.

Found %: N 8.31, 8.45; S 9.73, 9.60. $C_{17}H_{12}O_4N_2S$. Calculated %: N 8.23; S 9.41.

2-Hydroxymethyl-4-(p-nitrophenyl)-thiazole (II)

2-Benzoyloxymethyl-4-(p-nitrophenyl)-thiazole (25 g) was heated with 250 ml of a 5% alcoholic solution of potassium hydroxide until it had completely dissolved, and the hot solution was poured out into ice water. The crystalline precipitate which settled out was filtered off and recrystallized from alcohol. It consisted of shiny light yellow scales with a m.p. of 200°. The yield was 15.5 g (90%).

Found %: N 11.70, 11.71; S 13.30, 13.36. $C_{10}H_8O_3N_2S$. Calculated %: N 11.86; S 13.56.

2-Chloromethyl-4-(p-nitrophenyl)-thiazole (III)

a) 15 ml of thionyl chloride was added to a suspension of 14.2 g of 2-hydroxymethyl-4-(p-nitrophenyl)-thiazole in 50 ml of benzene, and the mixture was heated on a water bath at 75-80° for 2 hours. After distilling off the benzene and excess thionyl chloride in a vacuum, the residue was stirred into water, filtered, and washed several times with 5% sodium hydroxide solution and then with water, and after drying, was recrystallized from alcohol (with carbon). The yield of pure product was 9.6 g (63%). It consisted of light yellow needles with a m.p. of 157°.

Found %: N 10.70, 10.84; Cl 13.78, 13.82. $C_{10}H_7O_2N_2SCl$. Calculated %: N 11.00; Cl 13.94.

b) 17.7 g of 2-chloromethyl-4-phenylthiazole was added to 75 ml of concentrated sulfuric acid with cooling and stirring. A mixture of 19.5 ml of nitric acid (d 1.4) and 20 ml of concentrated sulfuric acid was added in the form of drops to the transparent solution obtained at 0-2° over a period of 30 minutes. After completion of the addition of the nitrating mixture, the stirring was continued for 30 minutes more at room temperature; the reaction mixture was then poured onto ice. The precipitate which settled out was filtered off, washed with water and dried. The yield of crude product was 19.9 g (93%). After recrystallization from alcohol or glacial acetic acid, light yellow needles with a m.p. of 157° were formed, which did not display melting point depression in a mixed sample with the product obtained from 2-hydroxymethyl-4-(p-nitrophenyl)-thiazole and thionyl chloride.

2-Ethoxymethyl-4-(p-nitrophenyl)-thiazole (IV)

0.6 g (0.025 g-atom) of sodium was dissolved in 20 ml of anhydrous alcohol, and 6.3 g (0.025 mole) of 2-chloromethyl-4-(p-nitrophenyl)-thiazole, in 100 ml of anhydrous alcohol, was then added to the solution. The mixture was heated on a boiling water bath for 8 hours, the alcohol was distilled off, and the residue was stirred into water, filtered off and recrystallized from alcohol. Preparation (V) was obtained analogously.

2-Aryloxymethyl-4-(p-nitrophenyl)-thiazoles (VI-IX)

A mixture, consisting of 5 g (0.02 mole) of 2-chloromethyl-4-(p-nitrophenyl)-thiazole, 0.04 mole of the corresponding phenol and 5.4 g (0.04 mole) of anhydrous potash in 75 ml of dry acetone, was boiled on a water bath for 18-20 hours. After the acetone had been distilled off, the residue was stirred into a 5% solution of sodium hydroxide, filtered off, washed with water and recrystallized from either alcohol or glacial acetic acid. The boiling point, yields and analytical data for the preparations obtained are set forth in Table 1.

The reduction of the 2-alkoxymethyl- and 2-aryloxymethyl-4-(p-nitrophenyl)-thiazoles and their conversion into the hydrochlorides and acetyl derivatives were carried out analogously to the preparation of the isomeric 4-alkoxymethyl and 4-aryloxymethyl compounds [1].

SUMMARY

1. A number of 2-alkoxymethyl- and 2-aryloxymethyl-4-(p-nitrophenyl)-thiazoles were prepared.

2. The 2-alkoxymethyl- and 2-aryloxymethyl-4-(p-aminophenyl)-thiazoles were prepared by reducing the nitrothiazoles formed.

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* T.p. = Consultants Bureau Translation pagination.

THE STRUCTURE OF GRAMICIDIN C

II. INVESTIGATION OF THE FORMATION OF THE COPPER COMPLEXES OF GRAMICIDIN

L. N. Akimova and N. I. Gavrilov

In the preceding work [1], we established the presence in gramicidin C of a piperazine ring which consists of proline and phenylalanine and proposed a hypothetical structure for this antibiotic. Nevertheless, a number of the properties of this interesting compound contradict the formula proposed: 1) the dimeric character of gramicidin; 2) the absence of carboxylic groups, or, more correctly, the impossibility of determining them by ordinary methods; 3) the formation of the "violet" copper complex with gradual appearance of the "red" complex and its reconversion into the "violet" complex when the biuret reaction is carried out a second time with the regenerated gramicidin; 4) the formation, when the copper complex of gramicidin with an absorption maximum at a wavelength of 535 mμ (which corresponds to that of an artificial mixture of complexes of 38% tripeptide and 62% pentapeptide) is decomposed, of a compound, the copper complex of which no longer gives the previous maximum, i.e., 535 mμ; a sort of regeneration in the properties of this compound occurs and the absorption maximum is restored to the initial value, i.e., to 570 mμ, and 5) the presence, in the hydrolysis products of gramicidin, of phenylalanylleucine, which also can not be explained by the monomeric formula proposed by us in the preceding article.

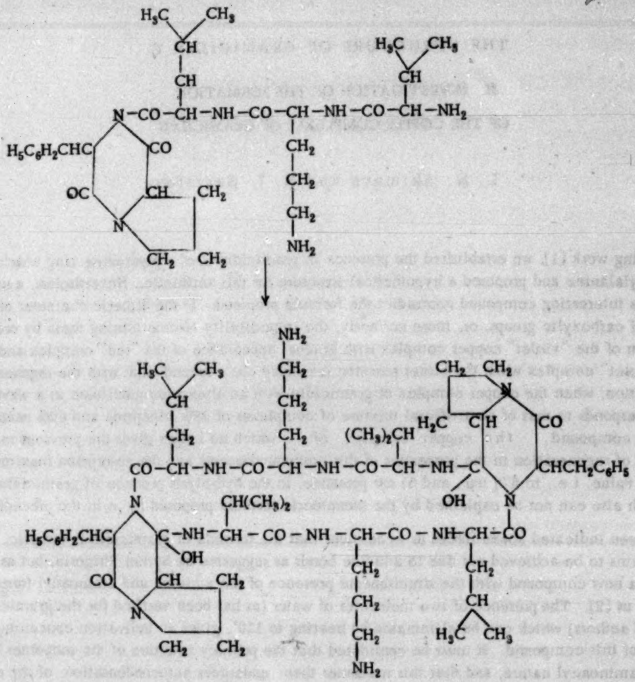
All that has been indicated above forces us to consider that the formula of gramicidin is dimeric, but that the dimerization seems to be achieved not due to amidine bonds as suggested by Syrkin-Shigorin, but as the result of the formation of a new compound with the simultaneous presence of the amidine and aminoacyl forms of the bonds discovered by us [2]. The presence of two molecules of water (as has been verified for the gramicidin molecule by a number of authors) which can be eliminated by heating to 110°, gives an indication concerning the mechanism of formation of this compound. It must be considered that the primary structure of the monomer has not an amidine, but an aminoacyl nature, and that this monomer then undergoes autocondensation, of the condensation type discovered by us for N-aminoacyldiketopiperazines with amines [2], as a result of which the hydrated form of the acylated amidine is obtained (Scheme 1).

The formula for gramicidin which is presented in the scheme is in accord with all the properties of gramicidin C known up to the present time, which have been revealed by both Soviet scientists (Gauze-Brazhnikova, Belozersky, Paskhina), and by foreign scientists (Senger, Singe, Gordon, Martin, Consden). The behavior of gramicidin C as a result of its treatment with alkali and with copper remains not entirely clear from the point of view of this formula. While the formation of the "violet" complex in the first instant of the biuret reaction follows from its structure, the additional appearance of the "red" complex requires explanation. The well-known opening of the ring in N-aminoacyldiketopiperazines when they are treated with copper in an alkaline medium is associated with lengthening of the chain. The possibility can not be excluded that the presence of a similar structure in gramicidin and the rupture of the piperazine ring associated with it is the cause of the "red" complex. However, the regeneration of this ring, after the isolation of gramicidin from the copper complex, is entirely unexpected and contains the clue to a number of facts in the field of protein chemistry which have hitherto remained unexplained.

When copper biuret complexes of proteins are decomposed by acidification and formed again through the action of an alkaline medium, they do not lose the capacity to yield primarily the "red" complex; when this is done with gramicidin we have a secondary appearance of the "red" complex. The structures depending on, and entering into, this complex, begin to compete with the structures of the "violet" complex only in the process of its formation, instantaneously disappearing upon acidification, so that it can arise again as a result of the action of alkali. The rupture of the piperazine ring during hydrolysis by acid, however, is demonstrated by the existence of leucylphenylalanine in the decomposition products (Singe and coworkers).

We have been trying to find a way to resolve all these still unsolved problems which are associated with the structure of gramicidin, the resolution of which will lead to the synthesis of this antibiotic. We can only state with certainty that: 1) in gramicidin C there is a piperazine ring, formed by phenylalanine and proline; 2) gramicidin C

Scheme 1



is a dimer: 3) in the native molecule of gramicidin there is a tripeptide which gives a complex with copper in alkaline medium with an absorption maximum at wavelengths of 570-575 mμ (Fig. 1); 4) as a result of more prolonged action of alcoholic alkali and copper on gramicidin C the "red" complex with an absorption maximum at a wavelength of 515 mμ is formed; this closely approaches the ordinary light absorption maximum (Fig. 2) for the pentapeptide (515 mμ) or the amide of the tripeptide (525 mμ); 5) after decomposing the copper biuret complex of gramicidin C, the gramicidin which is regenerated appears, with a high degree of probability to be identical with the initial gramicidin C, since: a) in the first instant of the biuret reaction, it gives the "violet" complex with an absorption maximum at wavelengths of 570-575 mμ; b) the copper biuret complex of gramicidin, after the prolonged action of alcoholic alkali on it, is characterized by a displacement of the absorption maximum in the direction of the short waves and appears to be the typical "red" complex; c) it gives a reaction with picric acid in soda solution which indicates the presence of a diketopiperazine ring; d) the melting point of the regenerated gramicidin is not depressed in a mixture with the initial gramicidin, and is equal to 282°, i.e., the melting point of the initial gramicidin;.6) the copper number of gramicidin is equal to 676, which is equivalent to half that of the dimeric form (1294). This indicates that gramicidin is not decomposed by the action of alkali, but that an as-yet-unknown rearrangement proceeds in it which gives equilibrium forms between the structures capable of forming the "violet" and "red" complexes. It is highly probable that gramicidin C has the structural formula set forth above.

EXPERIMENTAL

1. Preparation of the copper biuret solution of gramicidin. A weighed sample of gramicidin was dissolved in 50% alcohol; then an equal volume of 4% alcoholic alkali, and in the form of drops, a 25% alcoholic solution of $CuCl_2$ were added until flakes of cupric hydroxide which did not disappear were formed. The solution was shaken on a rocking device, and, after a specified interval, was centrifuged. The transparent solution of the

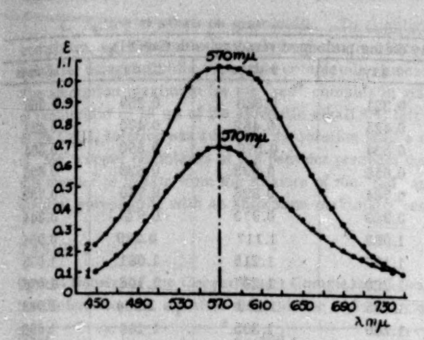


Fig. 1. Spectrophotometric curves of the copper biuret complexes. 1) 1% solution of gramicidin; 2) 0.01 M solution of the tripeptide.

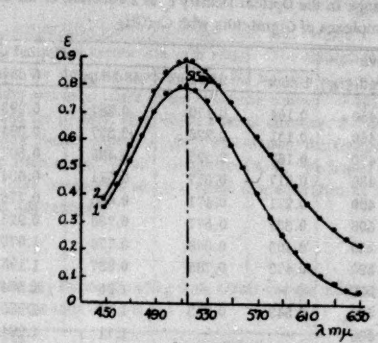


Fig. 2. Spectrophotometric curves of the copper biuret complexes. 1) 1% solution of gramicidin (after standing for 10 days with 2% NaOH); 2) 0.01 M solution of the pentapeptide.

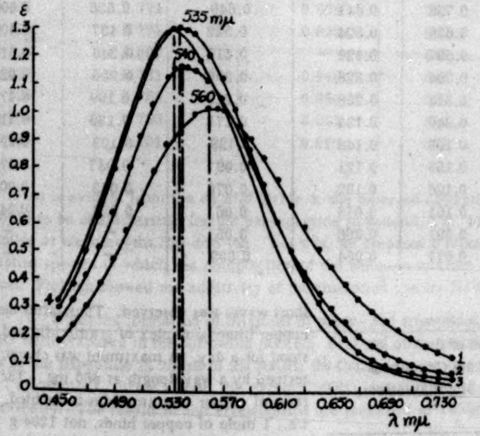


Fig. 3. Spectrophotometric curves of the copper biuret complexes of gramicidin (0.4% solution). 1) After standing for 24 hours with $Cu(OH)_2$; 2) after 48 hours; 3) after 5 days; 4) after standing for 15 days.

copper complex of gramicidin was diluted with 50% aqueous alcohol until the content of gramicidin was equal to 0.4%. The solution thus obtained was analyzed spectrophotometrically. An SF-4 spectrophotometer was used for taking the spectrophotometric curves.

2. Determination of copper in the copper biuret solutions of gramicidin. 10-20 ml of the centrifuged solution of the copper complex of gramicidin was burned with 4 ml of concentrated H_2SO_4, and transferred with 50 ml of water into a flask where the copper was determined iodometrically.

3. Investigation of the changes in gramicidin which depend on the time its copper solution stands with $Cu(OH)_2$. After the solution of the copper biuret complex of gramicidin had stood for 1 hour with $Cu(OH)_2$ it was centrifuged, investigated for its quantitative content of copper and analyzed spectrophotometrically (Fig. 3). The results of the determinations of copper and the spectrophotometric investigations of the copper biuret complexes of gramicidin are presented in Tables 1 and 2.

The investigations of the copper biuret complexes of gramicidin which we carried out led us to the conclusion that the properties of these complexes vary, and depend on the conditions under which they are formed. Thus, when the biuret reaction of gramicidin is carried out, in the first moment of the simultaneous addition of copper and NaOH, the formation of the "violet" complex of the tripepetide occurs. This is confirmed by the position of the maximum at wavelengths of 570-575 mμ, which is characteristic of the tripepetide (the copper determination was conducted simultaneously). However, even after standing for some time with excess cupric hydroxide, the displacement of the maximum in the direction of the

TABLE 1

Change in the Optical Density ϵ as a Function of the Duration of Standing of 0.4% Solutions of the Copper Biuret Complexes of Gramicidin with $Cu(OH)_2$

Wave length (mμ)	Optical density during prolonged standing with $Cu(OH)_2$							
	1 hour	24 hours	48 hours	5 days	7 days	9 days	13 days	15 days
450	0.104	0.170	0.257	0.293	0.321	0.363	0.359	0.358
460	0.131	0.226	0.327	0.394	0.425	0.462	0.470	0.421
470	0.167	0.296	0.425	0.507	0.534	0.576	0.550	0.504
480	0.217	0.377	0.511	0.634	0.656	0.693	0.638	0.636
490	0.271	0.471	0.645	0.776	0.784	0.826	0.760	0.732
500	0.331	0.577	0.736	0.925	0.923	0.973	0.878	0.844
510	0.403	0.688	0.774	1.070	1.063	1.117	0.989	0.954
520	0.472	0.783	0.887	1.198	1.197	1.215	1.081	1.078
525	–	–	1.03	1.256	1.220	1.267	1.106	1.078
530	0.543	0.883	1.06	1.283	1.265	1.293	1.134	1.088
535	–	–	1.11	1.294	1.280	1.305	1.146	1.098
540	0.605	0.943	1.13	1.294	1.274	1.302	1.126	1.080
550	0.649	0.998	1.12	1.281	1.217	1.245	1.075	1.028
560	0.683	1.020	1.08	1.202	1.127	1.149	0.987	0.944
570	0.690	0.999	1.02	1.105	1.020	1.035	0.880	0.838
575	0.690	0.958	–	–	–	–	–	–
580	0.680	0.905	0.921	0.981	0.894	0.904	0.743	0.724
590	0.651	0.838	0.824	0.862	0.775	0.775	0.654	0.608
600	0.606	0.759	0.723	0.738	0.641	0.640	0.538	0.500
610	0.562	0.673	0.626	0.618	0.524	0.522	0.437	0.400
620	0.510	0.521	0.527	0.507	0.420	0.412	0.340	0.312
630	0.453	0.449	0.430	0.394	0.326	0.306	0.256	0.222
640	0.403	0.386	0.357	0.314	0.258	0.229	0.199	0.172
650	0.353	0.332	0.293	0.249	0.194	0.171	0.139	0.119
660	0.312	0.287	0.242	0.198	0.148	0.129	0.109	0.098
670	0.268	0.252	0.202	0.155	0.121	0.097	0.067	0.076
680	0.242	0.222	0.171	0.126	0.102	0.076	0.043	0.061
690	0.212	0.198	0.142	0.101	0.078	0.061	0.029	0.048
700	0.187	0.169	0.127	0.091	0.066	0.051	–	–
710	0.167	0.152	0.105	0.077	0.054	0.039	–	–

TABLE 2

Ratio of Gramicidin and Copper in the Formation of the Complex and the Maximum Light Absorption of the Complexes as a Function of the Duration of Standing of the Biuret Solutions with $Cu(OH)_2$.

Duration of standing of copper complex with $Cu(OH)_2$	Amt. of gramicidin bound per mole of copper (g)	Ratio of copper to the substance (moles)	$\lambda_{max.}$ (mμ)
1 hour.	1.343	1:2	570
24 hours	688	1:1	560
48 hours	661.6	1:1	540
5 days.	682.1	1:1	535
7 days.	686.0	1:1	535
9 days.	686.0	1:1	535
13 days.	681.1	1:1	535

short waves was observed. Thus, after the copper biuret complex of gramicidin had stood for a day, its maximum was characterized by a wavelength at 560 mμ. The ratio of copper to gramicidin is doubled, i.e., 1 mole of copper binds, not 1294 g of gramicidin (maximum 570 mμ), but 688 g of gramicidin (maximum 560 mμ). Standing of the solution of the copper complex of gramicidin for 2 days caused a displacement of the maximum in the direction of the short waves by 20 mμ (maximum 540 mμ). The ratio of copper and gramicidin remained as before, i.e., if the molecular weight of gramicidin is considered as equal to 643, then this ratio is 1:1. In the fifth day of standing, the absorption maximum for the gramicidin complex was equal to 535 mμ, at the same ratio of copper to gramicidin. It is interesting to note that this maximum is preserved even after gramicidin has stood for 15 days with $Cu(OH)_2$.

4. Action of alkali on gramicidin. To establish the comparative quantities of the "red" and "violet" complexes, we undertook the analysis of the transformation products of gramicidin with alkali. The absorption maximum for the gramicidin tripeptide completely coincides with the absorption spectrum for the isolated tripeptide. The absorption maximum for the "red" complex in gramicidin was determined in the following manner: 0.1012 g of gramicidin in 10 ml of 2% alcoholic alkali was left to stand for 13 days, after which a small quantity (2-3 drops) of 2% $CuCl_2$ solution was added to the solution until a red color clearly appeared. As is well-known, the formation of "red" copper complexes of the peptides precedes the formation of the "violet" complexes [3, 4]. We hoped in this manner to isolate from the mixture of the "red" and "violet" complexes which is found in gramicidin, an individual polypeptide with an absorption maximum; our hope was realized.

TABLE 3

Optical Density of the Copper Biuret Complexes of Gramicidin (ϵ_1 During Standing with Alkali and the Addition of Insufficient Copper. ϵ_2 After the Addition of Excess Copper to the solution with ϵ_1)

Wave length (mμ)	ϵ_1 and ϵ_2		Wave length (mμ)	ϵ_1 and ϵ_2	
	0.9% solution	0.4% solution		0.9% solution	0.4% solution
450	0.346	0.314	540	0.673	0.946
460	0.428	0.404	550	0.592	0.896
470	0.520	0.502	560	0.504	0.832
480	0.619	0.604	570	0.413	0.754
490	0.701	0.714	580	0.322	0.682
500	0.771	0.808	590	0.254	0.602
510	0.791	0.892	600	0.191	0.526
515	0.800	–	610	0.149	0.454
520	0.781	0.946	620	0.116	0.388
525	0.765	0.956	630	0.077	0.322
530	0.733	0.962	640	0.061	0.294
535	0.701	0.962	650	0.054	0.244

As is evident from the data of Table 3, the observed absorption of the copper complex of gramicidin, ϵ_1, proved to be characteristic for the pentapeptide in general, i.e., 515 mμ,[*] in contrast to the tetrapeptide and octapeptide at wavelengths 520-525 mμ. For this, we prepared a mixture of the penta- and tripeptides, from the absorption spectra of which the composition of the unknown mixture can be determined by the position of the maximum. Plekhan showed the additivity of the absorption spectra for tetra- and tripeptides [4].

5. Complex formation of mixtures of penta- and tripeptides. Solutions of the biuret complexes of the peptides were prepared in the following fashion: 61.1 mg of the pentapeptide dissolved in 25 ml of 2% NaOH; 41.2 mg of the tripeptide in 25 ml of 2% NaOH; 2% $CuCl_2$ solution was added to the alkaline solutions of the peptides in 1 ml portions. After 1 hour, the excess $Cu(OH)_2$ was filtered off and the solution was analyzed spectrophotometrically. The results of the investigation are presented in Tables 4 and 5.

It follows from the data of the spectrophotometric observations of the individual complexes of this peptide (Fig. 4) that any mixture of the penta- and tripeptide forms a simple mixture of the complexes of these peptides. The absorption maxima for various mixtures of the tri- and pentapeptide are presented in Table 4. It follows from this summary table that the absorption maximum of solutions of the copper complexes of a mixture of 50% of the penta- and 50% of the tripeptide lies at a wavelength of 542.5 mμ, which corresponds to the arithmetical mean of the values of the maxima of these individual peptides.

If the percentage content of the tri- and pentapeptide in the mixture is plotted on the abscissa axis while the wavelength characteristic of the maximum absorption of the corresponding mixture is plotted on the ordinate axis, then a curve expressing the relationship of these quantities can be obtained (Fig. 4). By analyzing the curves of this mixture (Fig. 5) and comparing them with the curves of gramicidin (Figs. 6, 7 and 8), one can set up a certain representation of the decomposition of gramicidin as a function of time. The absorption maximum of

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[*] Further addition of copper to the solution with ϵ_1 until a hydrate formed caused a displacement of the absorption maximum to 535 mμ (ϵ_2).

TABLE 4

Composition of the Mixtures of Peptides

Expt. No.	Composition (in ml of 0.01 M peptide solutions)		Ratio of penta-peptide to tri-peptide (%)	λ max. (mμ)
	pentapeptide	tripeptide		
I	9	1	90:10	520
II	7	3	70:30	530
III	5	5	50:50	542.5
IV	3	7	30:70	555
V	2	8	20:80	562.5
VI	1	9	10:90	567.0
VII	10	—	100:0	515
VIII	—	10	0:100	572.5

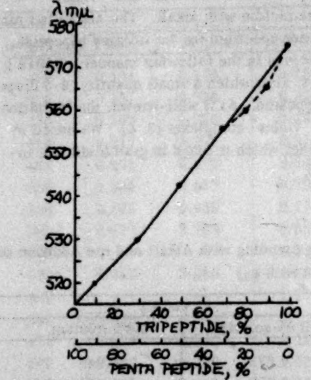

Fig. 4. Relationship between the content of penta- and tripeptides and the absorption maximum.

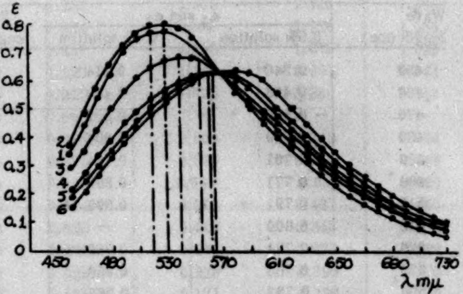

Fig. 5. Spectrophotometric curves of the copper biuret complexes of mixtures of the peptides (0.01 M solutions). 1) 70% penta- and 30% tripeptide; 2) 90% penta- and 10% tripeptide; 3) 50% penta- and 50% tripeptide; 4) 30% penta- and 70% tripeptide; 5) 20% penta- and 80% tripeptide; 6) 10% penta- and 90% tripeptide.

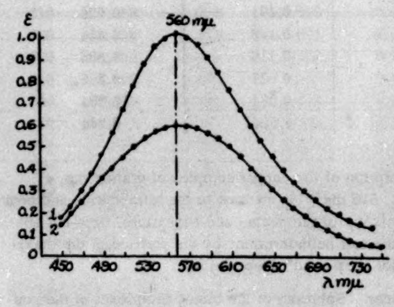

Fig. 6. Spectrophotometric curves of the copper biuret complexes. 1) 0.4% solution of gramicidin (after standing for 24 hours with $Cu(OH)_2$):2) a mixture of 30% pentapeptide and 70% tripeptide.

the copper complex of gramicidin lies at a wavelength of 535 mμ. According to the curve for the artificial mixture, this maximum corresponds with the maximum absorption by a solution of the copper complexes of a mixture of 62% of the pentapeptide and 38% of the tripeptide. Thus, by analyzing these curves, we have been able to verify the conversion of the "violet" copper complex into the "red" complex, or in other words, the profoundness of the isomerization of gramicidin.

6. Regeneration of gramicidin from the copper biuret complex. a) Preparation of the biuret solution of gramicidin for regenerating gramicidin from it. A solution of the copper biuret complex was prepared in the usual way from 1.6520 g of gramicidin, and, after it had stood for 7 days (absorption maximum 550 mμ), 15 ml of alcoholic alkali containing 2 g of NaOH was added to it. 3 days after the addition of the alkali, the copper complex was investigated; the copper was determined spectrophotometrically and quantitatively. The absorption maximum of this solution at a wavelength of 535 mμ, and the ratio of copper to the substance of 1:1 were constant for the final state of gramicidin in the copper complex. After the constants enumerated above had been reached, we proceeded to the regeneration of the gramicidin from the complex.

TABLE 5

Magnitudes of the Optical Densities ϵ of the Copper Biuret Complexes of Various Mixtures of Penta- and Tripeptides (the percentage contents in the mixtures of the penta- and tripeptides are set forth in Table 4)

Wave length (mμ)	Optical density							
	Sequence No.							
	I	II	III	IV	V	VI	VII	VIII
460	0.369	0.346	0.286	0.227	0.196	0.182	0.456	0.142
470	0.473	0.446	0.368	0.290	0.252	0.228	0.576	0.176
480	0.573	0.545	0.451	0.352	0.306	0.276	0.678	0.210
490	0.663	0.628	0.521	0.408	0.361	0.323	0.768	0.246
500	0.726	0.702	0.583	0.462	0.411	0.371	0.846	0.284
510	0.764	0.747	0.632	0.512	0.449	0.416	0.876	0.331
515	0.772	0.761	0.642	0.531	—	—	**0.888**	—
520	**0.775**	0.771	0.657	0.548	0.502	0.463	0.882	0.377
525	0.763	0.770	0.668	0.558	—	—	—	—
530	0.753	**0.772**	0.673	0.572	0.541	0.506	0.846	0.431
535	0.741	0.762	0.678	0.583	—	—	—	—
540	0.717	0.755	**0.679**	0.593	0.564	0.543	0.798	0.471
545	0.690	0.733	**0.679**	0.593	—	0.562	—	—
550	0.670	0.721	0.661	**0.602**	0.588	0.576	0.744	0.509
560	0.612	0.675	0.637	**0.602**	**0.598***	0.592	0.672	0.542
570	0.556	0.631	0.612	0.591	**0.593**	0.601**	0.612	0.556
575	—	—	—	—	—	—	—	**0.556**
580	0.503	0.582	0.576	0.582	0.579	0.592	0.546	0.554
590	0.443	0.528	0.539	0.544	0.561	0.580	0.418	0.552
600	0.397	0.482	0.497	0.515	0.532	0.552	0.444	0.518
610	0.355	0.437	0.455	0.473	0.498	0.520	0.396	0.496
620	0.317	0.394	0.410	0.431	0.460	0.478	0.360	0.459
630	0.267	0.335	0.351	0.378	0.403	0.421	0.276	0.413
640	0.242	0.298	0.312	0.334	0.361	0.366	0.258	0.375
650	0.215	0.263	0.270	0.287	0.311	0.331	0.216	0.322
660	0.187	0.228	0.232	0.244	0.263	0.272	0.186	0.281
670	0.164	0.197	0.196	0.203	0.222	0.227	0.161	0.242
680	0.146	0.171	0.164	0.168	0.183	0.188	0.152	0.202
690	0.126	0.144	0.135	0.139	0.151	0.154	0.141	0.166
700	0.108	0.123	0.112	0.114	0.127	0.127	0.129	0.142
710	0.093	0.104	0.092	0.091	0.104	0.103	0.108	0.115
720	0.081	0.087	0.074	0.074	0.083	0.068	0.091	0.094
730	0.070	0.074	0.061	0.058	0.066	0.066	0.083	0.076
740	—	—	—	—	0.055	0.054	—	0.064
750	—	—	—	—	0.045	0.044	—	0.052

b) Regeneration of gramicidin from the copper biuret complex. After it had stood for 10 days with $Cu(OH)_2$, and the maximum, which proved to be equal to 535 mμ, had been determined, the solution was centrifuged and poured off from the precipitate of $Cu(OH)_2$. 18% hydrochloric acid was added to the transparent solution of the copper biuret complex of gramicidin until the complex was decomposed. The precipitate which thereupon settled out consisted of needles under the microscope. The precipitate was diluted with water, centrifuged, washed three times with 50 ml (150 ml in all) of 4% hydrochloric acid and placed for drying in a desiccator over NaOH and $CaCl_2$.

c) Investigation by means of the biuret reaction of the regenerated gramicidin. 0.8180 g of the regenerated gramicidin was dissolved in 30 ml of 50% alcohol and 30 ml of a 4% alcoholic alkali solution, and 3 ml of a 25% alcoholic solution of $CuCl_2$ was added. The solution was stirred on a rocking device for 3 hours. The precipitate of cupric hydroxide was then centrifuged, and the colored solution of the biuret complex of regenerated

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* 565 mμ = 0.598.

** 565 mμ = 0.601.

TABLE 6

Magnitudes of the Optical Densities ε of Solutions of the Copper Biuret Complexes of Initial and Regenerated Gramicidin

Wave length (mμ)	Initial		Regenerated			
	concentration (%)					
	1.3	1.3	0.6	0.6	0.6	0.3
	duration of standing with $Cu(OH)_2$					
	7 days	10 days	3 hours	2 days	6 days	12 days
500	0.463	0.800	0.427	0.436	0.631	0.593
510	0.549	0.918	0.492	0.499	0.721	0.678
520	0.623	1.03	0.558	0.581	0.796	0.739
530	0.706	1.09	0.635	0.633	0.841	0.743
535	0.716	1.11	—	—	0.853	0.758
540	0.720	1.07	0.700	0.681	0.853	0.743
550	0.725	1.04	0.739	0.688	0.830	0.718
560	0.716	0.980	0.753	0.688	0.790	0.651
570	0.692	0.899	0.758	0.658	0.725	0.571
575	—	—	0.758	0.641	—	—
580	0.659	0.785	0.726	0.628	0.656	0.492
590	0.601	0.670	0.691	0.584	0.571	0.418
600	0.537	0.572	0.642	0.536	0.500	0.344

TABLE 7

Copper Numbers and Absorption Maxima of the Copper Biuret Complexes of Initial and Regenerated Gramicidin as a Function of the Duration of Standing with $Cu(OH)_2$

Duration of standing of the copper complex with $Cu(OH)_2$	Amt. of gramicidin bound per mole of copper (g)	Ratio of copper to the substance (moles)	$\lambda_{max.}$ (mμ)
Initial			
7 days.	752.1	1:1.2	550
10 days.	668	1:1	535
Regenerated*			
3 hours	1.427	2:1	570-575
2 days.	682	1:1	550
6 days.	676	1:1	535
12 days.	710	1:1	535

TABLE 8

Wave length (mμ)	Magnitude of the optical density ε of an 0.13% solution of the copper biuret complex of the reduced gramicidin
500	0.468
510	0.499
520	0.525
530	0.530
535	0.532
540	0.528
550	0.510
560	0.479
570	0.448
580	0.410
590	0.374
600	0.338

gramicidin was investigated for its quantitative content of copper as well as spectrophotometrically. The results of the determinations of copper and the spectrophotometric observations on the solutions of the copper biuret complexes of native and regenerated gramicidin are presented in Tables 6 and 7.

For the structure of gramicidin proposed by us, after the electroreduction, the presence in the solution of the tripeptide, valylornithylleucine, with an absorption maximum of the copper biuret complex at a wave length of 570-575 mμ, was to have been expected. After the electroreduction of the gramicidin, the solution formed a copper biuret complex with an absorption maximum at a wavelength of 535 mμ, which corresponds with the absorption maximum of a complex which includes four nitrogen atoms. This phenomenon can be treated as rupture of the amidine bond in the electroreduction process, with the tripeptide which is cleaved remaining still bound to the nitrogen of the piperazine ring and capable of forming a complex with copper with all four nitrogen atoms (three tripeptide nitrogen atoms and one nitrogen atom in the piperazine ring) (Table 8 and Scheme 2).

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* The gramicidin isolated contained 8.6% of moisture which was equivalent to approximately 3 molecules of water (mol. wt. 643).

The process of formation of the copper biuret complexes of gramicidin does not proceed at once, but takes time, and is considerably facilitated by mechanical agitation of the solution on a rocking device. The complex-formation of gramicidin is accelerated by increasing the concentration of alkali in the solution and by adding a sufficient quantity of alcohol, which facilitates the dissolving of gramicidin. This is evident from Tables 9 and 10.

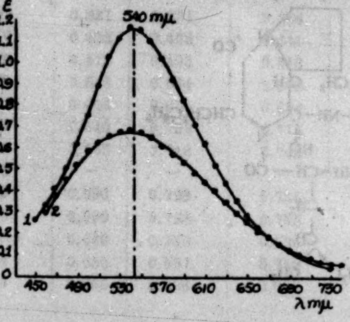


Fig. 7. Spectrophotometric curves of the copper biuret complexes. 1) 0.4% solution of gramicidin (after standing for 48 hours); 2) a mixture of 50% pentapeptide and 50% tripeptide.

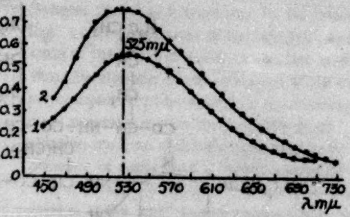


Fig. 8. Spectrophotometric curves of the copper biuret complexes. 1) 0.25% solution of gramicidin (after standing 41 hours with 10% NaOH); 2) mixture of 70% pentapeptide and 30% tripeptide.

It follows from the data of Table 10 that, as a result of the action of alkali on gramicidin neither in the presence of copper nor in its absence does decomposition of the molecules into the constituent parts, the amino acids or peptides, occur, but, rather, intramolecular rearrangement takes place. This rearrangement causes, in the formation of the copper complex, the use, in addition to the 3 nitrogen atoms which are included in the tripeptide, of the fourth nitrogen atom of the piperazine ring. As is evident from the table, the rate of the rearrangement depends on the concentration of alkali and the duration of the action. Thus, 2.5% alkali does not completely succeed in completing this rearrangement after 9 days, as is indicated by the copper number which is equal to 713.5, while 3.5% alkali completes the rearrangement in a shorter time (7 days). The action of 10% alkali on gramicidin completes the intramolecular rearrangement after a still shorter period (2 days).

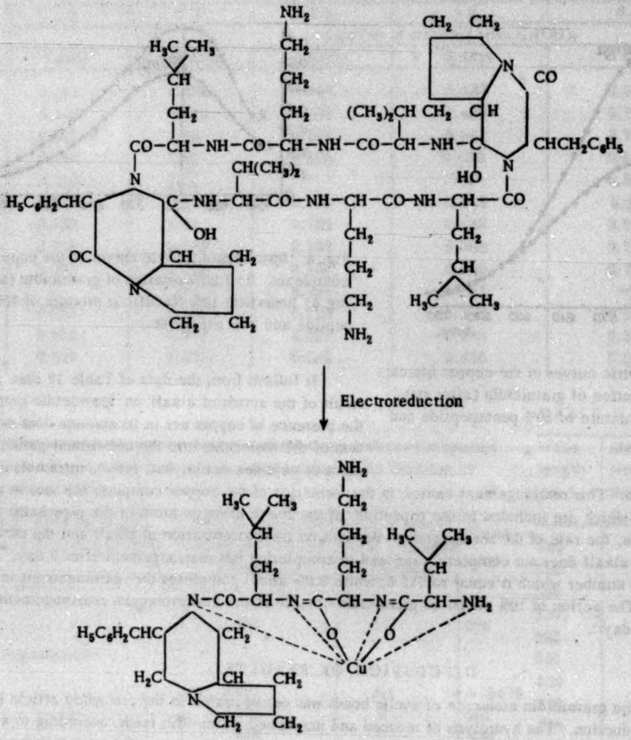
DISCUSSION OF RESULTS

The presence in the gramicidin molecule of cyclic bonds was demonstrated in the preceding article [1] by the method of electroreduction. The hydrolysis of reduced and unreduced gramicidin leads, according to a Van Slyke amine nitrogen determination, to the loss of 1 nitrogen atom occurring in a ring. This can only occur if the ring nitrogen is a proline nitrogen. The analysis of the interchange of amino acids performed by Singe and his coworkers showed the presence of a bond between proline and phenylalanine.

Numerous authors have isolated anhydrides consisting of proline and phenylalanine from the molecule of the initial proteins, which indicates the great probability of the formation of a cyclic bond between these two amino acids. It is, therefore, most probable to assume that there is a ring, consisting of phenylalanine and proline, in the gramicidin molecule, which is joined with the tripeptide. The sequence of aminoacids, established for gramicidin indicates that the composition of the tripeptide is valylornithylleucine. In the dimer of gramicidin, one of the tripeptides, according to our hypothesis, is joined with the piperazine ring by its carboxylic group at leucine, i.e., by an aminoacyl bond; while the amine group of valine of the second tripeptide has an amidine-like bond with the second phenylalanylprolinic diketopiperazine.

Thus, the dimeric structure of gramicidin C has the form presented in Scheme 2. As is evident from the scheme, the amidine bond is ruptured by electroreduction, and a trimethylenebenzylpiperazine, joined by an amide linkage with the leucine of the valylornithylleucine, is formed. The absorption spectrum of the copper complex in the thus-produced piperazine tripeptide will be found in the 515-535 mμ range. The compound can only exist in the first structural form (Scheme 3) in alkaline medium. When the solution of the copper biuret complex of gramicidin is acidified, it is instantaneously converted into its tautomeric form, in which both acyl groups, i.e.,

Scheme 2


Electroreduction

Copper complex of reduced gramicidin

TABLE 9

Change in the Optical Density ε as a Function of the Duration of Standing of 0.4% Solutions of the Copper Biuret Complexes of Gramicidin with $Cu(OH)_2$

Wave length (mμ)	Optical density during prolonged standing with $Cu(OH)_2$				
	1 hour	3 hours	4 hours	8 hours	24 hours
500	0.331	0.351	0.364	0.384	0.520
510	0.403	0.425	0.441	0.463	0.612
520	0.472	0.498	0.518	0.544	0.707
530	0.543	0.584	0.582	0.641	0.793
540	0.605	0.635	0.656	0.718	0.854
550	0.649	0.703	0.713	0.777	0.896
560	0.683	0.718	0.745	0.805	0.901
565	–	–	–	–	0.903
570	0.690	0.728	0.755	0.823	0.896
575	0.690	0.728	0.755	0.812	–
580	0.680	0.713	0.736	0.812	0.864
590	0.651	0.687	0.712	0.768	0.818
600	0.606	0.636	0.678	0.721	0.751

the tripeptides, migrate from the nitrogen of the piperazine ring to the exo-position of the amidine group.

The action of alkali in the absence or in the presence of copper shows that the initial gramicidin C is a tautomeric system (Scheme 3). This is confirmed by the following: 1) the appearance of the tripeptide spectrum of the biuret complex in alkaline medium (the slowness of the formation of the copper complex must be noted); 2) the rearrangement process proceeds more rapidly in an alkaline medium without copper than in the presence of copper and a weaker concentration of alkali. In the end, it leads to the formation of the "red" copper complex with an absorption maximum at a wavelength of 515 mμ.

TABLE 10

Copper Numbers and Absorption Maxima of Solutions of the Copper Biuret Complexes of Gramicidin as a Function of the Duration of Standing with $Cu(OH)_2$ and of the Concentration of Alkali*

Duration of standing of the complex with $Cu(OH)_2$	Concentration of alkali (%)	Gramicidin bound per mole of copper (g)	Ratio of copper to substance (moles)	$\lambda_{max.}$ (mμ)
1 hour.	1.5	1.343	1:2.08	570-575
3 hours		1.124	1:1.75	570-575
4 hours		1.045	1:1.64	570-575
8 hours		885.7	1:1.37	570
24 hours		824.1	1:1.28	565
24 hours	2.5	726.8	1:1.1	560
48 hours		726.8	1:1.1	540-545
5 days.		726.8	1:1.1	535-540
7 days.		720.1	1:1.1	535
9 days.		713.5	1:1.1	535
13 days.		691.1	1:1	535
7 days.	3.5	686.0	1:1	535
9 days.		686.0	1:1	535
13 days.		681.1	1:1	535
Biuret reaction of gramicidin after action of alkali alone				
2 days.	10	661.8	1:1	530-535
4 days.	10	636.3	1:1	525

The absorption maximum at a wavelength of 535 mμ characterizes an equilibrium mixture of the copper complexes with relative quantities of 38% of the "violet" and 62% of the "red" complex, which we established by analysis of a solution subjected to the action of alkali in the absence of copper, which gave, upon addition of copper (insufficient), the "red" complex with an absorption maximum at a wavelength of 515 mμ. This permitted us to set up an artificial mixture of pentapeptide with an absorption maximum at 515 mμ and of tripeptide with a maximum at 575 mμ. However, the use as a component source of the "red" complex of the pentapeptide (in the artifical mixture) does not imply at all that the appearance of this com-

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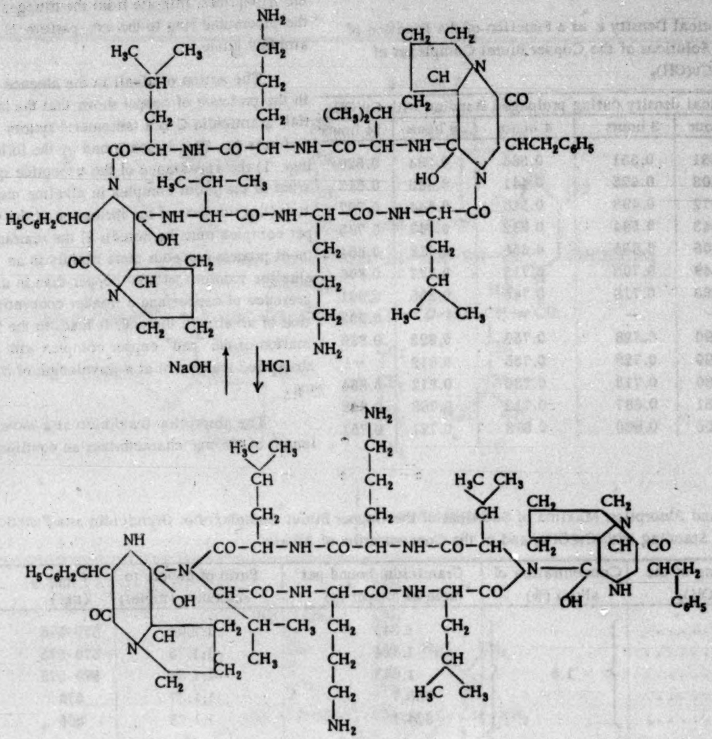
* The theoretical copper number of the gramicidin salt was equal to half its molecular weight, i.e., 607 + 36 = = 643. The total nitrogen was 13.25%.

Scheme 3



plex in gramicidin is due to opening of the piperazine ring with formation of the pentapeptide.

Rearrangement of the tripeptide (acyl) from the exo-nitrogen of the piperazine-amidine into the endo-position can create a structure in which the piperazine nitrogen, bound to the tripeptide is the nitrogen atom which creates the conditions for the formation of the "red" complex (amidic nitrogen).

Displacement of the absorption maximum toward the short waves has been observed in an amide–tripeptide complex [5] containing asparagine.

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* See Consultants Bureau Translation, page 371.

** See Consultants Bureau Translation, page 577.

*** See Consultants Bureau Translation, page 347.

**** See Consultants Bureau Translation, page 1675.

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INFLUENCE OF THE NATURE AND POSITION OF SUBSTITUENTS IN THE BENZENE RING ATTACHED TO NITROGEN ON THE CLOSING OF THE FIVE-MEMBERED HETEROCYCLIC RING IN ARYLAMIDES OF HYDROXYCARBOXYLIC ACIDS. XXI.

P. A. Petyunin, V. S. Shklyaev and I. S. Berdinsky

The influence of substituents in the phenyl radicals attached to carbinolic carbon on the closure of a heterocyclic ring in the arylamides of hydroxycarboxylic acids was elucidated in the preceding communications [1, 2]. The influence of the nature and position of the substituents in the benzene nucleus attached to nitrogen on the closure of a five-membered heterocyclic ring was studied in the present work.

Since, due to the rapidly condensing arylamide groups, it is practically impossible to detect the influence of substituents in the benzene nucleus attached to nitrogen on the closure of a heterocyclic ring [3], we have concerned ourselves with the arylamides of 4,4'-dimethoxybenzilic acid, since the ring in them is closed maximally slowly [1]. The experiments were carried out according to methods previously described [1]. In setting up a single experiment, we took 1 ml of a solution of 0.015 mole of the arylamide in 1 liter of glacial acetic acid and 0.1 ml of concentrated sulfuric acid. The results of the experiments are presented in the table. The rate of closure of the five-membered heterocyclic ring in the anilide of 4,4'-dimethoxybenzilic acid (Arylamide No. 1), equal to 3.5 minutes, was taken as the unit.

Practically equivalent electrophile reaction centers were contained in all the compounds set forth, since identical substituents were found in the phenyl radicals near the carbinol atom. Consequently, the difference in the readiness of closure of the five-membered ring in the arylamides of 4,4'-dimethoxybenzilic acid can be explained only by differences in the electron donor properties of the benzene nucleus attached to nitrogen.

TABLE

Rate of Closure of the Five-Membered Heterocyclic Ring in Arylamides of 4,4'-Dimethoxybenzilic Acid

Arylamide No.	Formula	Rate of closure of the ring at 60°
1	$C_6H_5NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	1
2	$o\text{-}CH_3C_6H_4NHCO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	0.32
3	$m\text{-}CH_3C_6H_4-NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	2.34
4	$p\text{-}CH_3C_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	1.17
5	$o\text{-}CH_3OC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	0.88
6	$m\text{-}CH_3OC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	3.5
7	$p\text{-}CH_3OC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	1.75
8	$p\text{-}ClC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	0.06
9	$p\text{-}BrC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	0.12
10	$p\text{-}IC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	0.17
11	$p\text{-}(CH_3)_2NC_6H_4NH-CO-C(OH)(C_6H_4OCH_3\text{-}p)_2$	Did not close

The influence of the nature of the substituents on the closure of the ring is evident in the cases of condensation of arylamides Nos. 1, 4, 7, 8, 9, 10 and 11. The rate ofring closure is increased by the introduction of electron donor substituents (Arylamides Nos. 4 and 7). Under the influence of halogens attached to nitrogen (Arylamides Nos. 8, 9 and 10), the benzene nucleus is deactivated, and the rate of cyclization is lowered by 6-15 times.

The unsuccessful attempt to close the heterocyclic ring in Arylamide No. 11 is to be explained by the manifestation of a strong deactivating effect on the part of the electron acceptor $(CH_3)_2\overset{+}{N}H$ group. The formation of the latter is quite probable, since the condensation proceeded with the aid of sulfuric acid. However, in the p-dimethylaminoanilide of benzilic acid, the halochromic salt of which contains a more electrophilic carbonium carbon, the heterocyclic ring is closed rather readily [4].

From the point of view of the position of the substituents (Arylamides Nos. 2-7), the rate of ring closure falls in the order: m > p > o. In the meta-isomers (Arylamides Nos. 3 and 6), the electron donor substituents increase the electron density at the loci of condensation, which facilitates the closure of the ring. In the para-isomers (Arylamides Nos. 4 and 7), the rate of ring closure is diminished, since the orienting influence of the amidic nitrogen and the substituent do not coincide. Finally, in the ortho-isomers (Arylamides Nos. 2 and 5), due to the manifestation of steric hindrance on the part of the substituent, the displacement of the unshared electron pair of the amide nitrogen on the benzene nucleus is diminished [5], which is reflected in a considerable lowering of the rate of ring closure.

EXPERIMENTAL

Ethyl ester of m-methyloxanilic acid. 17 g of m-toluidine and 29.2 g of diethyl oxalate were placed in a flask equipped with a fractionating column and a downward condenser. The contents of the flask were heated on a sand bath; under these conditions, 8 ml of the reaction alcohol (theoretically, it should have been 9.2 ml) was distilled off. Upon cooling, the reaction mass was poured out into 50 ml of alcohol. 1.5 g of the di-m-toluidide of oxalic acid with a m.p. of 127-129° was filtered off. The literature data give the m.p. as 131° [6].

The ethyl ester of m-methyloxanilic acid was isolated by diluting the filtrate with water; the m.p. was 60-61°. The yield was 6 g (18.3%). It was converted into the well-known amide of m-methyoxanilic acid with a m.p. of 187-189° [6] by the action of ammonia.

m-Toluidide of 4,4'-dimethoxybenzilic acid. 4.5 g of the m-methyloxanilic ester was added to the p-anisylmagnesium iodide obtained from 25.7 g of p-iodoanisole and 2.64 g of magnesium in 100 ml of ether. The reaction mass was heated for 1 hour on a water bath and decomposed with a saturated solution of ammonium chloride. The reaction product was isolated by the usual method. It consisted of colorless needles (from alcohol) with a m.p. of 142-142.5°. The yield was 4 g (48.3%). The product dissolved in alcohol, ether, benzene and acetic acid. It gave a raspberry-red color, with concentrated H_2SO_4, which disappeared upon prolonged standing or heating.

0.2486 g sub.: 13.6 ml 0.05 N H_2SO_4. 0.3584 g sub.: 18.9 ml 0.05 N H_2SO_4. Found %: N 3.81, 3.67. $C_{23}H_{23}O_4N$. Calculated %: N 3.72.

p-Toluidide of 4,4'-dimethoxybenzilic acid. The starting materials were 8 g of the ethyl ester of p-methyloxanilic acid, 35 g of p-iodoanisole and 3.6 g of magnesium. It consisted of crystals (from acetic acid) with a m.p. of 159-161°. It was quite soluble in glacial acetic acid and difficultly soluble in benzene, toluene, ether and alcohol. It formed a reddish-violet color with concentrated H_2SO_4 which disappeared upon heating. The yield was 8 g (56%).

0.2044 g sub.: 10.9 ml 0.05 N H_2SO_4. 0.3140 g sub.: 15.7 ml 0.05 N H_2SO_4. Found %: N 3.73, 3.51. $C_{23}H_{23}O_4N$. Calculated %: N 3.72.

o-Toluidide of 4,4'-dimethoxybenzilic acid. 5.6 g of o-methyloxanilic ester, 31.4 g of p-iodoanisole and 3.24 g of magnesium were taken in the reaction. It consisted of plates (from alcohol) with a m.p. of 161-163°. The yield was 10.5 g (50%). It was quite soluble in acetic acid, benzene and alcohol and was difficultly soluble in ether and gasoline. It dissolved in concentrated H_2SO_4 with the formation of a raspberry color which disappeared upon heating or prolonged standing.

0.2614 g sub.: 13.9 ml 0.05 N H_2SO_4. 0.2264 g sub.: 11.5 ml 0.05 N H_2SO_4. Found %: N 3.69, 3.55. $C_{23}H_{23}O_4N$. Calculated %: N 3.72.

p-Chloranilide of 4,4'-dimethoxybenzilic acid. The p-chloranilide of 4,4'-dimethoxybenzilic acid was prepared from 5.2 g of p-chlorooxanilic ester, 23.4 g of p-iodoanisole and 2.4 g of magnesium. It consisted of colorless crystals (from alcohol) with a m.p. of 124-126°. The yield was 4.5 g (51.9%). It was quite soluble in the ordinary organic solvents. With sulfuric acid, it gave a raspberry color, which disappeared on heating.

0.2424 g sub.: 12.3 ml 0.05 N H_2SO_4. 0.2149 g sub.: 11 ml 0.05 N H_2SO_4. Found %: N 3.56, 3.58. $C_{22}H_{20}O_4NCl$. Calculated %: N 3.53.

p-Bromoanilide of 4,4'-dimethoxybenzilic acid. The starting materials were 6.9 g of p-bromooxanilic ester, 23.4 g of p-iodoanisole and 2.4 g of magnesium. It consisted of lentil-shaped crystals (from 80% acetic acid) with a m.p. of 112-114°. The yield was 7 g (62.5%). It was soluble in alcohol, acetic acid, toluene and ether and was difficultly soluble in gasoline. The solution in sulfuric acid was raspberry colored and was decolorized on heating.

0.2125 g sub.: 9.24 ml 0.05 N H_2SO_4. 0.2610 g sub.: 11.05 ml 0.05 N H_2SO_4. Found %: N 3.05, 2.96. $C_{22}H_{20}O_4NBr$. Calculated %: N 3.17.

p-Iodoanilide of 4,4'-dimethoxybenzilic acid. The reaction was carried out between p-anisylmagnesium iodide obtained from 23.4 g of p-iodoanisole, 2.4 g of magnesium in 100 ml of ether, and 7.2 g of p-iodooxanilic ester. It consisted of plates (from alcohol) with a m.p. of 127.5-130.5°. The yield was 5 g (45.4%). It was quite soluble in ether, benzene and acetic acid, and difficultly soluble in gasoline. With concentrated H_2SO_4 it formed a raspberry color, which disappeared on heating.

0.3111 g sub.: 13.8 ml 0.05 N H_2SO_4. 0.2382 g sub.: 10.4 ml 0.05 N H_2SO_4. Found %: N 3.1, 3.07. $C_{22}H_{20}O_4NI$. Calculated %: N 2.86.

p-Dimethylaminoanilide of 4,4'-dimethoxybenzilic acid. 7 g of p-dimethylaminooxanilic ester, 28.1 g of p-iodoanisole and 2.9 g of magnesium were taken in the reaction. It consisted of plates (from alcohol) with a m.p. of 165-166°. The yield was 6 g (50%). It was soluble in acetic acid, alcohol and toluene, and difficultly soluble in ether. With concentrated H_2SO_4, it gave a stable raspberry color, which did not disappear upon heating.

0.2801 g sub.: 27.6 ml 0.05 N H_2SO_4. 0.1930 g sub.: 19.3 ml 0.05 N H_2SO_4. Found %: N 6.9, 7.0. $C_{24}H_{26}O_4N_2$. Calculated %: N 6.88.

p-Anisidide of 4,4'-dimethoxybenzilic acid. The starting materials were 29.3 g of p-iodoanisole, 3 g of magnesium and 5.6 g of p-methoxyoxanilic ester. It consisted of needles (from toluene) with a m.p. of 99-101°. The yield was 6.3 g (64%). With concentrated H_2SO_4, it gave a raspberry color, which disappeared on heating.

0.266 g sub.: 13.3 ml 0.05 N H_2SO_4. 0.2068 g sub.: 10.6 ml 0.05 N H_2SO_4. Found %: N 3.5, 3.58. $C_{23}H_{23}O_5N$. Calculated %: N 3.56.

m-Anisidide of 4,4'-dimethoxybenzilic acid. 5 g of m-methoxyoxanilic ester, 25.4 g of p-iodoanisole and 2.64 g of magnesium were taken in the reaction. It consisted of plates (from benzene) with a m.p. of 120-121° (with decomposition). The substance melted on heating and then solidified anew and again melted at 200°. The yield was 4.7 g (57.3%). It was soluble in alcohol, acetic acid and benzene. It gave a disappearing raspberry color with concentrated H_2SO_4.

0.2146 g sub.: 10.4 ml 0.05 N H_2SO_4. 0.1886 g sub.: 10.1 ml 0.05 N H_2SO_4. Found %: N 3.38, 3.73. $C_{23}H_{23}O_5N$. Calculated %: N 3.56.

3,3-Bis(4-methoxyphenyl)-5-methyloxindole. 3 ml of concentrated H_2SO_4 was added to a solution of 4 g of the p-toluidide of 4,4'-dimethoxybenzilic acid in 20 ml of glacial acetic acid. The reaction mass was heated on a water bath (60-70°) until the raspberry color disappeared and, after cooling, was poured out into 50 ml of water. It consisted of rods collected in nodules (from benzene + gasoline), m.p. 188-189°. The yield was 3 g (78.5%).

0.2035 g sub.: 11.2 ml 0.05 N H_2SO_4. Found %: N 3.82. $C_{23}H_{21}O_3N$. Calculated %: N 3.90.

3,3-Bis-(4-methoxyphenyl)-5-methoxindole. The starting materials were 4 g of the p-anisidide of 4,4'-dimethoxybenzilic acid dissolved in 15 ml of glacial acetic acid, and 3 ml of concentrated H_2SO_4. It consisted of octahedra (from alcohol) with a m.p. of 221.5-222°. The yield was 2.6 g (68%).

0.2342 g sub.: 12.9 ml 0.05 N H_2SO_4. Found %: N 3.84. $C_{23}H_{21}O_4N$. Calculated %: N 3.74.

3,3-Bis-(4-methoxyphenyl)-5-bromooxindole. 3,3-Bis-(4-methoxyphenyl)-5-bromooxindole was prepared by adding 3 ml of concentrated H_2SO_4 to a solution of 3 g of the p-bromoanilide of 4,4'-dimethoxybenzilic acid in 15 ml of glacial acetic acid. It consisted of plates (from toluene) with a m.p. of 214-215°. 1.9 g (66.1%) was obtained.

0.1665 g sub.: 7.8 ml 0.05 N H_2SO_4. 0.1713 g sub.: 7.7 ml 0.05 N H_2SO_4. Found %: N 3.18, 3.14. $C_{22}H_{18}O_3NBr$. Calculated %: N 3.30.

3,3-Bis-(4-methoxyphenyl)-5-iodooxindole. 3.5 g of the p-iodoanilide of 4,4'-dimethoxybenzilic acid and 3 ml of concentrated H_2SO_4 were taken in the reaction. It consisted of lentil-shaped crystals (from alcohol) with a m.p. of 221-222°. The yield was 2.9 g (86.2%).

0.1538 g sub.: 6 ml 0.05 N H_2SO_4. 0.3261 g sub.: 14 ml 0.05 N H_2SO_4. Found %: N 2.73, 3.00. $C_{22}H_{18}O_3NI$. Calculated %: N 2.97.

3,3-Bis-(4-methoxyphenyl)-7-methyloxindole. The starting materials were 2 g of the o-toluidide of 4,4'-dimethoxybenzilic acid and 2 ml of concentrated H_2SO_4. It consisted of prisms (from glacial acetic acid) with a m.p. of 240-242°. The yield was 1.2 g (63%).

0.1229 g sub.: 6.5 ml 0.05 N H_2SO_4. 0.1500 g sub.: 8.4 ml 0.05 N H_2SO_4. Found %: N 3.70, 3.92. $C_{23}H_{21}O_3N$. Calculated %: N 3.90.

3,3-Bis-(4-methoxyphenyl)-5-chlorooxindole. 3,3-Bis-(4-methoxyphenyl)-5-chlorooxindole was prepared by the intramolecular condensation of 0.8 g of the p-chloroanilide of 4,4'-dimethoxybenzilic acid with the aid of 0.5 ml of concentrated H_2SO_4. It consisted of rods (from toluene) with a m.p. of 197.5-198°. The yield was 0.45 g (59%).

0.1520 g sub.: 8 ml 0.05 N H_2SO_4. Found %: N 3.68. $C_{22}H_{18}O_3NCl$. Calculated %: N 3.70.

SUMMARY

1. The influence of the nature and position of the substituents attached to nitrogen in the benzene nucleus, on the closure of the five-membered heterocyclic ring in the arylamides of 4,4'-dimethoxybenzilic acid was studied; it was established under these conditions that the rate of ring closure under the influence of the various substituents diminishes in the following order: $CH_3O > CH_3 > I > Br > Cl > (CH_3)_2\overset{+}{N}H$.

Depending on the position of the substituents, the rate of condensation falls in the sequence: m > p > o.

2. A number of the arylamides of 4,4'-dimethoxybenzilic acid, which were derived from 3,3-bis-(4-methoxyphenyl)-oxindole and which had not been described in the literature, were prepared and their properties studied.

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RHODANO-SUBSTITUTED (ISOTHIOCYANATE-SUBSTITUTED) SILANES

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Rhodano-substituted silanes were prepared for the first time as early as 1877 by Miquel [1], who prepared tetrarhodanosilane by the reaction of silicon tetrachloride with lead thiocyanate. This author ascribed the structure of tetrathiocyanatosilane to the tetrarhodanosilane. Reynolds [2] subsequently prepared tetrarhodanosilane by this method and studied certain of its properties and transformations. He also considered that this compound had the tetrathiocyanatosilane $Si(SCN)_4$ structure.

Anderson, in a number of his works [3-11], described the synthesis of many rhodano-substituted silanes of the $R_nSi(NCS)_{4-n}$ type, where the R-alkyl is phenyl, chlorine or an alkoxy group and n = 1-3. The general method of preparing these compounds which Anderson used was based on the exchange reaction of the corresponding chlorosilanes R_nSiCl_{4-n} with silver thiocyanate. In his first works, Anderson [3-5] ascribed to the rhodano-substituted silanes the structure of thiocyanate derivatives, $R_nSi(SCN)_{4-n}$. Subsequently, Anderson [7], as a result of comparing the molecular refractions of the rhodano-substituted silanes which he had prepared with those described in the literature for derivatives of thiocyanic and isothiocyanic acid, became convinced that their structure rather corresponds to that of isothiocyanates, $R_nSi(NCS)_{4-n}$. Nevertheless, certain authors [12, 13], even at the present time, describe the rhodanosilanes as derivatives of thiocyanic acid.

Eaborn [14] showed that triethylrhodanosilane is formed in an excellent yield by the reaction of triethylsilane with silver thiocyanate according to the scheme:

$$(C_2H_5)_3SiH + AgNCS \longrightarrow (C_2H_5)_3SiNCS + Ag + \tfrac{1}{2} H_2.$$

He also prepared triethyl- and trimethylrhodanosilanes by a series of exchange reactions of R_3SiX derivatives with silver thiocyanate:

$$R_3SiX + AgNCS \longrightarrow R_3SiNCS + AgX$$
$$(R = C_2H_5,\ CH_3,\ \ X = Cl,\ Br,\ I,\ CN,\ R_3SiS).$$

There is also a brief indication in the literature [15] that triphenylrhodanosilane can be obtained by the reaction of triphenylchlorosilane with the thiocyanates of silver, lead and ammonia, or with thiourea.

According to patent data [12, 16], rhodano-substituted silanes find application for imparting hydrophobic properties to various materials. In addition, as we have found, certain of these compounds have insecticide and fungicide activity.

Setting as our goal the synthesis and study of the properties of rhodano-substituted silanes, we tested a number of methods of preparing them which were based on the exchange reaction of the corresponding chlorosilanes with the thiocyanates of silver, lead, copper, potassium, sodium and ammonium. Coming to the conclusion that all the indicated rhodanides more or less readily enter into the exchange reaction with chloro-substituted silanes, we concerned ourselves with ammonium thiocyanate, since it is the cheapest and reacts smoothyl and readily (somewhat better results were given only by the expensive silver thiocyanate). Even on merely stirring dry ammonium thiocyanate with any chloro-substituted silane, an energetic reaction proceeds, and a 10-minute heating of the reaction mixture is sufficient for complete replacement of all the chlorine atoms by the thiocyanate group. However, it is expedient to conduct the synthesis of rhodano-substituted silanes from the indicated reagents in a boiling benzene medium, which leads to higher yields and purer products.

The physical properties of the compounds obtained by us and the analytical data are presented in Table 1.

The method of determining the physical constants has been described in one of our works [17]. The boiling points were determined at pressures close to normal pressure (± 5 mm) and converted to 760 mm by the approximate formula $t_{760} = t_p - 0.00012(t_p + 273)(p - 760)$, which is correct for non-associated organic substances

TABLE 1

Properties of Thiocyanato-Substituted Silanes

Formula	B.p. at 760 mm (± 0.5°)	B.p. at the given pressure (± 1°)	M.p. (± 0.5°)	d_4^{20}	n_D^{20}	MR_D		Analysis (%)				Yield (%)
						found	calc'd	NCS		Si		
								found	calc'd	found	calc'd	
$Si(NCS)_4$	313.8°	182° (15)	143.8°	1.41	–	–	–	89.20 89.11	89.21	10.68 10.72	10.79	82
$CH_3Si(NCS)_3$	267.5	146 (15)	72.0	1.30	–	–	–	80.30 80.32	80.16	12.90 12.79	12.92	75
$C_2H_5Si(NCS)_3$	276.5	151 (15)	–	1.2658	1.6195	64.17	64.18	75.32 75.10	75.30	12.15 12.02	12.14	73
$C_3H_7Si(NCS)_3$	289.2	160 (14)	–	1.2248	1.6016	68.70	68.82	71.02 71.18	71.00	11.31 11.36	11.44	69
iso-$C_3H_7Si(NCS)_3$	279.1	157 (14)	16.5	1.2158	1.6050	69.52	68.94	71.00 70.93	71.00	11.27 11.35	11.44	61
$C_4H_9Si(NCS)_3$	298.8	166 (15)	−0.4	1.1888	1.5927	73.93	73.46	67.20 67.33	67.16	10.90 10.86	10.83	71
$C_6H_5Si(NCS)_3$	–	151 (2)	52.2	1.30	–	–	–	62.17 62.09	62.36	10.00 10.17	10.05	70
$C_6H_5CH_2Si(NCS)_3$	–	169 (2)	36.0	1.28	–	–	–	59.20 59.19	59.38	9.82 9.76	9.57	63
$(CH_3)_2Si(NCS)_2$	217.5	101 (15)	18.0	1.1416	1.5675	49.91	49.90	66.53 66.61	66.64	16.00 16.03	16.11	73
$(C_2H_5)_2Si(NCS)_2$	245.5	– –	–	1.0937	1.5546	59.35	58.91	57.57 57.61	57.40	13.70 13.65	13.88	80
$(C_4H_9)_2Si(NCS)_2$	–	154.5 (6)	–	0.9950	1.5106	77.77	77.49	45.08 45.16	44.94	10.52 10.61	10.87	52
$(CH_3)_3SiNCS$	143.8	– –	−33.0	0.9308	1.4809	40.13	40.13	44.12 44.32	44.25	21.37 21.30	21.40	72
$(C_2H_5)_3SiNCS$	210.5	– –	–	0.9385	1.4948	53.85	53.65	33.55 33.63	33.51	16.43 16.11	16.20	60
$(C_4H_9)_3SiNCS$	–	137.5 (2)	–	0.9063	1.4893	82.05	81.51	22.39 22.28	22.56	10.87 11.06	10.91	55

when the precision of the boiling point determination does not exceed + 0.05°.*

We consider that the rhodanides of silicon have the structure of isothiocyanatosilanes $R_nSi(NCS)_{4-n}$. This is clear even from a comparison of the boiling points of analogously constructed organic and silicoorganic compounds which are presented in Table 2.

The isothiocyanate structure of rhodanosilanes is also confirmed by their formation in excellent yields by the reaction of isocyanosilanes with elementary sulfur [19] according to the scheme:

$$R_3SiNC + S \rightarrow R_3SiNCS.$$

All the isothiocyanato-substituted silanes described by us consisted of colorless or slightly yellowish liquids or crystalline solids, stable to heating, with a sharp odor, which were readily hydrolyzed by water. Even traces of moisture were sufficient to cause the coloring of these compounds as a consequence of hydrolysis. When the rhodano-substituted silanes which were sufficiently liquid to form drops or vapors came in contact with the skin, they colored it dark red. On the other hand, the trialkylisothiocyanatosilanes, beginning with $(C_2H_5)_3SiNCS$, do not have a sharp odor and are hydrolyzed very slowly by water. The isothiocyanatosilanes also readily react with organic compounds containing labile hydrogen (alcohols, amines and acids) with the evolution of thiocyanic acid.

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* For associated organic compounds (alcohols, acids, phenols, etc.) and water, $t_{760} = t_p - 0.00010(t_p + 273)(p - 760)$.

EXPERIMENTAL

All the initial alkyltrichlorosilanes and dialkyldichlorosilanes were synthesized by the reaction of the corresponding organo magnesium compounds with excess silicon tetrachloride. The trialkylchlorosilanes were prepared by our method [18] by the reaction of the corresponding hexaalkyldisiloxanes with aluminum chloride. All the initial chlorosilanes were purified by fractional distillation in a column with a packing of ceramic rings with an efficiency of 40 theoretical plates. Their constants, which are presented in Table 3, are in excellent agreement with the literature data.

TABLE 2

Boiling Point in °C

X	$(CH_3)_3CX$ (T_1)	$(CH_3)_3SiX$ (T_2)	T_2-T_1
OCH_3 . . .	54	57	3
OC_2H_5 . .	70	75	5
F.	12	16	4
Cl	52	58	6
Br	72	80	8
I.	100	107	7
NCS.	140	144	4
SCN.	> 150	–	–

TABLE 3

Properties of the Initial Alkylchlorosilanes and $SiCl_4$

Formula	B.p. at 760 mm (± 0.2°)	d_4^{20}	n_D^{20}
$SiCl_4$	57.0	1.481	–
CH_3SiCl_3.	66.1	1.275	–
$C_2H_5SiCl_3$.	100.5	1.2373	1.4256
n-$C_3H_7SiCl_3$	125.0	1.1965	1.4314
iso-$C_3H_7SiCl_3$	119.5	1.1948	1.4330
n-$C_4H_9SiCl_3$	149.0	1.1609	1.4368
n-$C_5H_{11}SiCl_3$	169.2	1.1330	1.4400
$C_6H_5SiCl_3$.	201.1	1.324	1.5247
$C_6H_5CH_2SiCl_3$	95.8*	1.288	1.5258
$(CH_3)_2SiCl_2$	70.1	1.0745	1.4055
$(C_2H_5)_2SiCl_2$	130.0	1.0519	1.4313
(n-$C_4H_9)_2SiCl_2$	212.0	0.9912	1.4449
$(CH_3)_3SiCl$	58.0	0.8580	1.3885
$(C_2H_5)_3SiCl$	146.5	0.8968	1.4313
(n-$C_4H_9)_3SiCl$	128.5*	0.8793	1.4472

The initial chemically pure ammonium thiocyanate was ground into a fine powder and dried for 10 days in a vacuum over phosphoric anhydride. The benzene, used as a solvent, was fractionally distilled over sodium.

All the syntheses of cyanato-substituted silanes were carried out by a uniform method under conditions which excluded the advent of moisture from the air (absorption bottle with concentrated sulfuric acid). The liquid isothiocyanate-substituted silanes obtained were purified by fractional distillation in a column with a glass packing with an efficiency of 15 theoretical plates, while the solid isothiocyanate substituted silanes were purified by recrystallization from benzene or petroleum ether. They were analyzed by titration of the thiocyanic acid which formed upon hydrolysis with 0.1 N NaOH in a water-alcohol medium in the presence of phenolphthalein as the indicator. The silicon was determined by the method of wet combustion.

The syntheses of several isothiocyanate-substituted silanes are presented below as examples.

Synthesis of tetraisothiocyanatosilane. 38.1 g (0.5 mole) of ammonium thiocyanate, 150 ml of dry benzene and 17.0 g (0.1 mole) of silicon tetrachloride were placed in a round-bottomed flask, equipped with a reflux condenser. The reaction mixture was boiled for 4 hours and filtered while hot. The precipitate was washed several times with hot benzene. The greater part of the benzene was distilled off from the filtrate. The crystals of tetraisothiocyanatosilane which precipitated on cooling were separated and washed with cold benzene. The yield was 21.3 g, or 82% of the theoretical, calculating on the basis of the initial silicon tetrachloride. After a repeated recrystallization from benzene, the tetraisothiocyanatosilane obtained had the constants presented in Table 1.

Synthesis of butyltriisothiocyanatosilane. A solution of 28.7 g (0.15 mole) of butyltrichlorosilane in 150 ml of benzene and 38.1 g (0.5 mole) of ammonium thiocyanate was boiled with a reflux condenser for 3 hours. The precipitate of ammonium salts was filtered off and washed with hot benzene. The benzene was distilled off from the filtrate and the residue vacuum distilled. The yield of butyltriisothiocyanatosilane with a b.p. of 182-188° (31 mm) was 29.8 g (71%).

Synthesis of dimethyldiisothiocyanatosilane. A solution of 25.6 g (0.2 mole) of dimethyldichlorosilane in 100 ml of benzene was boiled with 32.0 g (0.42 mole) of ammonium thiocyanate for 3 hours. The precipitate of ammonium salts was filtered off and washed with hot benzene. The benzene was distilled off from the filtrate, and the residue distilled. The yield of dimethyldiisothiocyanatosilane with a b.p. of 211-215° was 24.0 g (73%).

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* At 10 mm.

Synthesis of triethylisothiocyanatosilane. A mixture of 30.1 g (0.2 mole) of triethylchlorosilane and 19.0 g (0.25 mole) of ammonium thiocyanate was heated to boiling for 10 minutes, after which it was distilled. At 190-205°, 27 g of distillate came over which contained a suspension of sublimed ammonium salts. It was again distilled and, after filtration, gave 20.8 g (60%) of triethylisothiocyanatosilane with a b.p. of 205-210°.

The yield of triethylisothiocyanatosilane was raised to 72% by conducting the reaction in a benzene medium.

SUMMARY

The reaction of ammonium rhodanide (ammonium thiocyanate) with the corresponding chloro-substituted silanes led to the synthesis of 14 isothiocyanato-substituted silanes $R_nSi(NCS)_{4-n}$ ($\underline{n} = 0$-3); their physical properties were described.

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INVESTIGATION OF CERTAIN CONVERSIONS OF ABIETIC ACID

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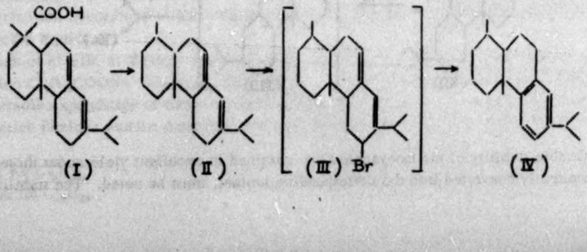
Abietic acid (I), due to its accessibility and chemically interesting hydrophenanthrene structure, has been the subject of many investigations. Certain of them had the object of finding an application for it in fine organic synthesis. The closeness of the structure of abietic acid to that of a number of valuable medicinal preparations was the reason the first investigations were directed toward utilizing it for the preparation of physiologically active substances. Thus, 6-hydroxydehydroabietinol with estrogenic activity, 6-aminodehydroabietinol and its N-dimethyl derivative to which morphine-like action [1] was ascribed, were synthesized.

Information concerning the use of abietic acid in perfumery is limited to the indication that certain of its derivatives (the methyl ester, its tetrahydro derivative and certain other derivatives) are fixing agents for perfumes. Both abietic acid itself and its derivatives are odorless; this appears to be a general property of compounds which contain 20 and more carbon atoms. This circumstance has been continuously associated with exploratory works involving the synthesis of perfumes on the basis of abietic acid with the necessary reduction in the number of carbon atoms in its molecule.

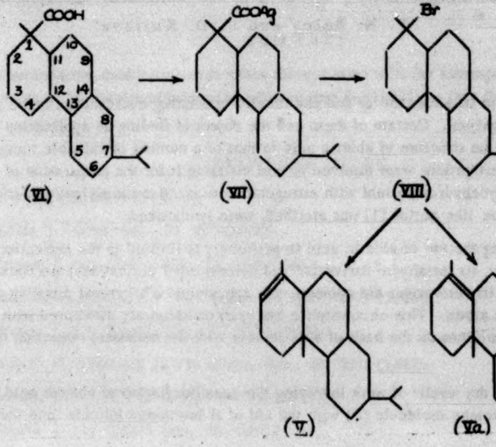
In the present article, the results of work involving the decarboxylation of abietic acid, attempts to introduce a bromine atom into the abietene molecule (II) with the aid of N-bromosuccinimide, and the synthesis of tetrahydroabietin are reported.

To prepare abietene from abietic acid we tried heating it with water, sodium hydroxide and dimethylaniline. It turned out that, in the latter case, the anhydride of abietic acid is formed, the decarboxylation of which anhydride proceeds at a temperature above 300°. The decarboxylation of (I) in the presence of water under pressure takes place in a temperature range which excludes any side reactions. However, on heating abietic acid for 24 hours at a heating oven temperature of 260-280°, it is only 10-13% converted into hydrocarbons. A more convenient preparative method for obtaining abietene proved to be the decarboxylation of the sodium salt of abietic acid with the composition $C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$ in the presence of a small quantity of alkali (2-3% of the weight of the salt). As a result of heating the reaction mixture for 4 hours at a temperature of 230-250°, abietene was obtained in a yield of 40% of the theoretical. The constants of substance (II), prepared from substance (I) by decarboxylation with water, only varied within a small range: d_4^{20} 0.9605-0.9640, n_D^{20} 1.5285-1.5296. The properties of abietene, obtained by the decarboxylation of the salt, were still more constant. In both cases they were in accord with the literature data [2-6].

The study of the reaction of abietene with N-bromosuccinimide showed that the bromo-derivative which is thereby formed, to which we assigned the structure of bromoabietene (III), is very unstable. It can be detected, but not, as a consequence of its decomposition during purification, isolated, except in those experiments which are carried out at a temperature not above 0°. If the reaction of (II) with N-bromosuccinimide is carried out in the presence of heating, then HBr is isolated from the reaction mixture; under these conditions the bromide (III) initially formed is almost completely converted into the hydrocarbon (IV), i.e., the result of the reaction is dehydrogenation. After distilling over NaOH, dehydroabietene (IV) was obtained in the pure form:

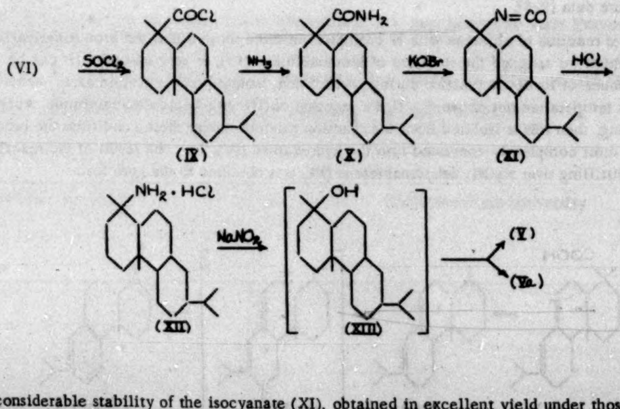


We initially tried to accomplish the synthesis of tetrahydroabietin, with a double bond in position 1,2 (V), or 1,11 (Va), according to the scheme:



We did not succeed in doing this, as we assumed, because it was impossible to carry out the projected synthesis in stages with isolation of the bromide (VIII). The temperature conditions necessary for the reaction between (VII) and Br_2 in the direction of forming (VIII) (Borodin reaction [7]) are apparently very close to those under which the dehydrobromination of (VIII) into the unsaturated hydrocarbon (V or Va) proceeds. In view of the presence in the reaction medium of Br_2, this hydrocarbon undergoes various further conversions, which lead, in the end, to the formation of a mixture of hydrocarbons and bromo-derivatives.

We succeeded in accomplishing the synthesis of tetrahydroabietin from tetrahydroabietic acid (VI) according to another scheme:



The considerable stability of the isocyanate (XI), obtained in excellent yield under those conditions in which other amides are directly converted into the corresponding amines, must be noted. The stability of (XI) enabled us to isolate it from the reaction mixture and to purify it in an appropriate manner (m.p. 59-60° from 50% alcohol).* The hydrochloride of tetrahydroabietylamine (XII) was obtained from it by heating with concentrated HCl; the use of solvent proved not to be obligatory in this reaction.

It is also necessary to note that in the last stage of the synthesis, we did not succeed in any of the experiments in isolating even a small quantity of a substance with an alcoholic character from the reaction mixture. The sole product of this reaction was tetrahydroabietin (V or Va).

Uncertainity as to the structure of the hydrocarbon obtained by us can arise in connection with the fact that the similar conversion of primary amines is often accompanied by isomerization. However, for example, in the study of the reaction of the secondary amine – methylcyclopropylaminomethane – with HNO_2, Demyanov and Pinegin [9] noted an almost quantitative formation of methylcyclopropylcarbinol. They advanced a hypothesis concerning the interrelation of this phenomenon (the absence of isomerization) with the presence of a second radical located on the carbon atom with the NH_2 group.

In our case, the conversion of (XII) into (V) or (Va), apparently, also proceeds without change in the structure of the carbon skeleton, and consequently through a stage of the tertiary, readily-dehydratable alcohol (XIII). To characterize the hydrocarbon (V) or (Va), it was subjected to catalytic hydrogenation over platinum catalyst. The quantity of H_2 absorbed corresponded to the presence in its molecule of one double bond. The hydrocarbon corresponded to tetrahydroabietene in physical constants and in the data from its elementary analysis.

EXPERIMENTAL

Preparation of abietic acid. 100 g of finely ground rosin (acid number 166.5) was vacuum distilled for 2 hours. 74.7 g of distillate (yield 83.2%, calculating on the basis of the acidic part of the rosin) was obtained:

B.p. 234-240° (3.5 mm), softening temperature 75°, acid number 184.2.

100 g of the distillate was recrystallized from acetone and alcohol and 37.7 g of abietic acid (yield 37.9%, calculating on the basis of the acidic part of the distillate) was obtained:

M.p. 154-157°, α_D^{20} −69.6° (alcohol), acid number 185.3, thiocyanometric bromine number 47.54.**

Decarboxylation of abietic acid by heating with water. 20 g of abietic acid (m.p. 154-157°) and 100 ml of water were placed in a 200 ml rotating autoclave. The mixture was heated for 24 hours at a temperature of the heating oven of 260-280°. Upon cooling, the water layer was separated and the viscous oil was dissolved in ether. The extract was washed with 5% sodium hydroxide, and with water, and dried with sodium sulfate. The residue after distilling off the solvent was vacuum distilled over metallic sodium. 2.2 g (12.8%) of the hydrocarbon was obtained:

B.p. 167-170° (3.5-4 mm), thiocyanometric bromine number 70.8, n_D^{20} 1.5285, d_4^{20} 0.9605, MR_D 82.91,*** 82.27.**** $C_{19}H_{30}\ulcorner_2$. Calculated 82.41; EMR_D 0.5. $C_{19}H_{28}\ulcorner_3$ Calculated 81.94; EMR_D 0.33.

12.84 mg sub.: 44.86 mg CO_2; 13.81 mg H_2O. 13.05 mg sub.: 42.45 mg CO_2; 12.89 mg H_2O. Found %: C 88.39, 88.71; H 11.16, 11.05. $C_{19}H_{30}$. Calculated %: C 88.31; H 11.69. $C_{19}H_{28}$. Calculated %: C 88.99; H 11.01.

Preparation of the salt of abietic acid with the composition $C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$. 66 g of rosin (acid number 166.5) and 134 g of alcohol were placed in a three-necked flask with a stirrer, a reflux condenser and a dropping funnel. 100 g of 3% HCl was added to the boiling solution; it was boiled for 15 minutes, and 20 g of a solution which contained 3.3 g of NaOH was added. After 5 minutes, 50 g more of a solution containing 19.6 g of NaOH was added. After 24 hours the solution was filtered and the precipitate was washed with alcohol and dried. 145.8 g of the salt (yield, calculating on the basis of the acidic part of the rosin, 61.8%) with a m.p. of 172-175°, was obtained.

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* The considerable stability of the isocyanates of the resin acids has been noted in one of the patents [8], in which their characterization is confined to the indication that the isocyanates of abietic, dehydro- and dihydroabietic acids are viscous liquids.

** A purer preparation of abietic acid (m.p. 170-174°, α_D^{20} −98.70°) was obtained by purification via the sodium salt of the composition $C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$, but since such a purification was associated with large losses of material and considerable expenditure of time, we considered it possible to use preparations corresponding in their properties to those which Ruzicka and his coworkers had used in their works, in which the structure of abietic acid was elucidated.

*** At mol. wt. 258 for $C_{19}H_{30}$.

**** At mol. wt. 256 for $C_{19}H_{28}$.

Decarboxylation of the acid sodium salt of abietic acid. 43 g of the dry salt with the composition $C_{19}H_{29}COONa \cdot 3C_{20}H_{30}O_2$ and 1 g of NaOH were placed in a 200 ml round-bottomed flask. After heating for 4 hours at a reaction mixture temperature of 230-250°, the contents of the flask were dissolved in ether, washed with 5% NaOH and with water, and dried with sodium sulfate. After distilling off the solvent, the residue was vacuum distilled over metallic sodium. 3.6 g (40.2%) of the hydrocarbon was obtained. It consisted of a colorless, odorless, viscous oil which was quite soluble in the ordinary solvents and insoluble in water:

B.p. 164-171° (1.5-2 mm), thiocyanometric bromine number 73.39, n_D^{20} 1.5289, d_4^{20} 0.9616, MR_D 82.87;* 82.22.** $C_{19}H_{30}\digamma_2$. Calculated 82.41; EMR_D 0.46. $C_{19}H_{28}\digamma_3$. Calculated 81.94; EMR_D 0.28.

12.47 mg sub.: 40.29 mg CO_2; 29.97 mg H_2O. 13.47 mg sub.: 43.61 mg CO_2; 13.77 mg H_2O. Found %: C 88.29, 88.11; H 11.44, 11.64. $C_{19}H_{30}$. Calculated %: C 88.31; H 11.69. $C_{19}H_{28}$. Calculated %: C 88.99, H 11.01.

Reaction of abietene with N-bromosuccinimide. 4.7 g (0.02 mole) of N-bromosuccinimide (m.p. 173°) and 15 ml of CCl_4 (anhydrous) were placed in a 100 ml two-necked flask with a stirrer and a dropping funnel. A solution of 6.8 g (0.02 mole) of abietene with a b.p. of 160-163° (1 mm) in 25 ml of the same solvent was added in the form of drops to the mixture, which was cooled to 0°. It was stirred at a temperature of 0° for 3 hours, the succinimide was filtered off, and the CCl_4 was distilled off in a vacuum at a bath temperature which did not exceed 20°: 4.8 g of an oil which was soluble in the ordinary organic solvents was obtained.

The product contained 24.53% Br (by the Stepanov method). $C_{19}H_{29}Br$. Calculated %: Br 23.69.

After distilling over NaOH, 1.21 g of the substance was obtained:

B.p. 118-120° (0.1-0.2 mm), n_D^{20} 1.5339, d_4^{20} 0.9679, MR_D 82.34, calculated 81.94. Literature data for dehydroabietene: b.p. 113° (0.1 mm, $n_D^{20.5}$ 1.540, b.p. 112° (0.06 mm), 180-182° (11 mm); $n_D^{17.5}$ 1.5370 [10], b.p. 180° (12 mm), n_D^{25} 1.5354 [11].

Tetrahydroabietic acid. 500 g of finely ground rosin (acid number 166.5) was hydrogenated in a three-liter autoclave over 50 g of pyrophoric nickel under a pressure of 200-207 atm and at a temperature of 210-230°. 66.9 liters of hydrogen was absorbed in 3.5 hours. Upon cooling, the hydrogenation product was dissolved in benzene, the catalyst was filtered off, and after distilling off the solvent, the residue was vacuum distilled. 354.2 g of distillate (yield 77.9%, calculating on the basis of the acid part of the rosin) was obtained:

B.p. 192-205° (0.3-0.5 mm), softening temperature 80°, acid number 179.4.

After two-fold recrystallization from acetone, 155.1 g of tetrahydroabietic acid (yield 42.9%, calculating on the basis of the acid part of the distillate, and 34.1%, on the initial rosin) was obtained:

M.p. 165-168°, acid number 183.3, thiocyanometric bromine number 0; mixed sample with abietic acid melted at 113-117°.

16.27 mg sub.: 46.91 mg CO_2; 16.53 mg H_2O. 15.17 mg sub.: 43.56 mg CO_2; 15.32 mg H_2O. Found %: C 78.62, 78.30; H 11.37, 11.30. $C_{20}H_{34}O_2$. Calculated %: C 78.36; H 11.19.

It consisted of colorless shiny needles, collected in rosettes, which were readily soluble in ether, benzene and toluene, soluble in acetone, alcohol and glacial acetic acid, and insoluble in water.

Silver salt of tetrahydroabietic acid. A solution of 5.0 g (0.016 moles) of tetrahydroabietic acid (m.p. 165-168°, thiocyanometric bromine number 0), in 50 ml of 96% alcohol was titrated with 5% aqueous NaOH. While the solution was being stirred vigorously, a solution of 3.0 g (0.017 mole) of $AgNO_3$ in 120 ml of water was added and the mixture stirred for 20 minutes. The precipitate was filtered off, washed, dried at 100° and then at 2-3 mm over P_2O_5. 6.2 g of the salt (73%), with a m.p. of 165-168° was obtained.

120.8 mg sub.: 31.0 mg Ag. Calculated: 30.1 mg Ag.

Acid chloride of tetrahydroabietic acid. 10.0 g (0.03 mole) of tetrahydroabietic acid (m.p. 165-168°) and 11.0 g (0.09 mole) of $SOCl_2$ were placed in a round-bottomed flask (50 ml) with a reflux condenser. After 30 minutes, the excess $SOCl_2$ was distilled off and 10.3 g (97%) of the substance was obtained. After two-fold recrystallization from acetone, the m.p. was 69-69.5°.

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* At mol. wt. 258 for $C_{19}H_{30}$.

** At mol. wt. 256 for $C_{19}H_{28}$.

22.397 mg sub.: 0.688 ml 0.01 N $Hg(NO_3)_2$/0.1 g sample . 24.939 mg sub.: 0.770 ml 0.01 N $Hg(NO_3)_2$/ 0.1 g sample . Found %: Cl 10.90, 10.95. $C_{20}H_{33}OCl$. Calculated %: Cl 10.91.

It consisted of colorless shiny crystals in the form of elongated ellipsoids which were readily soluble in benzene, ether and acetone, poorly soluble in alcohol, and insoluble in water.

Amide of tetrahydroabietic acid. A suspension of 10 g of technical grade acid chloride of tetrahydroabietic acid and 150 ml of an aqueous solution of ammonia (d 0.86 at 0°) was shaken for 8 hours. The precipitate was filtered off, washed with water, and dried over calcium chloride. 8.6 g (92%) of a product with a m.p. of 182-183° was obtained (the melting point did not change upon recrystallization from alcohol).

14.4 mg sub.: 41.4 mg CO_2; 15.06 mg H_2O. 13.7 mg sub.: 39.5 mg CO_2; 14.1 mg H_2O. 19.94 mg sub.: 0.879 ml N_2 (21°, 738 mm). 21.84 mg sub.: 0.859 ml N_2 (22°, 737 mm). Found %: C 78.40, 78.63; H 11.70, 11.52; N 4.97, 4.93. $C_{20}H_{35}ON$. Calculated %: C 78.63; H 11.55; N 4.58.

It consisted of colorless crystals which were readily soluble in benzene, toluene, ether, hot alcohol and acetone, poorly soluble in cold alcohol and acetone, and insoluble in water.

Tetrahydroabietylisocyanate. 5.0 g (0.01 mole) of the finely ground amide of tetrahydroabietic acid (m.p. 182-183°), 50 ml of water and 53 g of potassium hypobromite, prepared from 5.2 g (0.03 mole) of bromine and 52 ml of 25% aqueous potassium hydroxide at a temperature of −5°, were placed in a round-bottomed 250 ml flask with a reflux condenser. The mixture was heated for 2 hours at a temperature of 65-70°. The tetrahydroabietylisocyanate was extracted with ether, the ethereal solution was washed with water and dried over sodium sulfate. The residue, after distilling off the solvent, was vacuum distilled. 4.6 g (84.4%) of a substance with a b.p. of 199-202° (3-4 mm) was obtained. After two-fold recrystallization from 50% alcohol, the m.p. was 59-61°.

15.0 mg sub.: 43.5 mg CO_2; 15.1 mg H_2O. 15.6 mg sub: 45.4 mg CO_2; 15.4 mg H_2O. 17.9 mg sub.: 0.769 ml N_2 (21°, 742 mm). 17.94 mg sub.: 0.750 ml N_2 (23°, 758 mm). Found %: C 79.08, 79.36; H 11.27, 11.05; N 4.87, 4.70. $C_{20}H_{33}ON$. Calculated %: C 79.15; H 10.96; N 4.62.

It consisted of fine shiny needles which were readily soluble in benzene, ether, toluene, hot acetone and alcohol, slightly soluble in cold alcohol, and insoluble in water.

Hydrochloride of tetrahydroabietylamine. 1.2 g of tetrahydroabietylisocyanate (m.p. 59-61°) and 6 ml of HCl (d 1.18) were placed in a 50 ml round-bottomed flask with a reflux condenser. The mixture was boiled for 15 minutes. The crystals which formed on cooling were filtered off, washed with anhydrous ether and dried. 1.05 g (84.6%) of the hydrochloride was obtained. After recrystallization from hot water, the m.p. was 152-153°.

24.939 mg sub.: 0.779 ml 0.01 N $Hg(NO_3)_2$ / 0.1 g sample. 21.170 mg sub.: 0.684 ml 0.01 N $Hg(NO_3)_2$ / 0.1 g sample. 18.74 mg sub.: 0.758 ml N_2 (24°, 745 mm). 17.44 mg sub.: 0.690 ml N_2 (24°, 746 mm). Found %: Cl 11.33, 11.18; N 4.56, 4.46. $C_{19}H_{36}NCl$. Calculated %: Cl 11.29; N 4.46.

It consisted of fine crystals which were soluble in hot water, cold alcohol, poorly soluble in cold water, and insoluble in acetone and benzene.

Tetrahydroabietylamine picrate, m.p. 219-221°, consisted of shiny yellow crystals in the form of rectangles, which were soluble in alcohol, acetone and benzene, and insoluble in water.

14.54 mg sub.: 1.46 ml N_2 (18°, 728 mm). 6.94 mg sub.: 0.70 ml N_2 (22°, 730 mm). Found %: N 11.28, 11.31. $C_{25}H_{38}O_7N_4$. Calculated %: N 11.05.

Tetrahydroabietin. 7.0 g (0.02 mole) of tetrahydroabietylamine (m.p. 152-153°), 70 ml of water and a solution of 2.3 g (0.03 mole) of $NaNO_2$ in 23 ml of water were placed in a 250 ml two-necked flask with a reflux condenser. The mixture was heated for 1 hour. After cooling, it was extracted with ether, and the ethereal solution was washed with dilute H_2SO_4 and then with water and dried over sodium sulfate. The residue after distilling off the solvent was vacuum distilled. 3.5 g (60.3%) of the hydrocarbon was obtained:

B.p. 178-179° (3-4 mm); n_D^{20} 1.5190, d_4^{20} 0.9537, MR_D 82.86, calculated 82.86.

13.4 mg sub.: 43.0 mg CO_2; 15.2 mg H_2O. 19.9 mg sub.: 63.8 mg CO_2; 22.2 mg H_2O. Found %: C 87.51, 87.43; H 12.69, 12.48. $C_{19}H_{32}$. Calculated %: C 87.60; H 12.40.

It consisted of a viscous, odorless oil which was readily soluble in the ordinary organic solvents and insoluble in cold carbon tetrachloride and water.

Tetrahydroabietene. A solution of 1.5 g of tetrahydroabietin with a b.p. of 175-177.5° (2-3 mm) in 15 ml of anhydrous alcohol was hydrogenated at atmospheric pressure over Pt which had been prepared by the reduction of 0.3 g of PtO_2. The hydrogenation was continued for 50 hours, in the course of which the calculated quantity of hydrogen (137 ml) was absorbed. After eliminating the catalyst, the solvent was distilled off and the residue was vacuum distilled. 1.1 g (72.8%) of the following fraction was obtained:

B.p. 178-182° (8-9 mm), n_D^{20} 1.5060, d_4^{20} 0.9362, MR_D 83.29, calculated 82.34.

Literature data [11]: b.p. 179-180° (12 mm), d_4^{20} 0.9374, n_D^{20} 1.5025. The tetrahydroabietene, obtained by the hydrogenation of abietin, had a b.p. of 183-184° (12 mm), d_4^{20} 0.9368, n_D^{20} 1.5022.

14.0 mg sub.: 44.8 mg CO_2; 15.9 mg H_2O. 12.9 mg sub: 41.83 mg CO_2; 14.8 mg H_2O. Found %: C 87.26, 87.31; H 12.71, 12.84. $C_{19}H_{34}$. Calculated %: C 86.94; H 13.01.

SUMMARY

1. It was shown that heating abietic acid with water under pressure at a temperature of 230-250° yields abietene with a yield of 12-13%. Decarboxylation of the acid sodium salt of abietic acid in the presence of a small quantity of alkali proceeds at the same temperature and yields abietene with a yield of 40%.

2. It was established that the bromide, formed by the reaction of abietene with N-bromosuccinimide, is unstable at temperatures above 0° The result of this reaction appears to be the dehydrogenation of abietene.

3. The synthesis of tetrahydroabietin was accomplished according to the following scheme: tetrahydroabietic acid → the acid chloride of tetrahydroabietic acid → the amide of tetrahydroabietic acid → → tetrahydroabietylisocyanate → the hydrochloride of tetrahydroabietylamine → tetrahydroabietin.

4. The preparation of tetrahydroabietin as a result of the reaction of the hydrochloride of tetrahydroabietylamine with nitrous acid indicates that isomerization of the ring does not occur in the process of replacing the amino group with a hydroxy group.

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MENDELEEV'S CLASSIFICATION OF THE ELEMENTS*

(A brief report of the paper which was read and discussed at the colloquium of the Platinum Division of the Institute of General and Inorganic Chemistry of the Academy of Sciences USSR, July 13 and 20, 1950, and at the session of the section of the Scientific Council of the Platinum Division, the Institute of General and Inorganic Chemistry of the Academy of Sciences USSR held June 5, 1951)

A. I. Mashentsev

As is well-known, D. I. Mendeleev saw the distribution of the rare-earth metals in the periodic system as "one of the most difficult problems" presented by the periodic law [1]. He acknowledged a second complication for group VIII, in the series of which there are three elements each. He also indicated the indefiniteness of the position of hydrogen as the "lightest" element. The evolution of the periodic system of elements (1869-1905) of D. I. Mendeleev [2] which proceeded from then on, led to its division into four parts, in connection with the introduction of the rare-earth and thorite actinide metals. The number of series of the system was simultaneously reduced. Then, with the "generalization" of the elements of groups 0 and VIII, it became impossible to avoid discontinuities in all the periods, to wit: between the halogens and the inert gases [3], or, in other cases, between the elements of groups VII and VIII [4]. After rejection of the Mendeleevian even and uneven series and subdivision the elements of each group into two "subgroups", proposed by L. Meyer [5], arbitrary changes in the composition of these "subgroups", for example, in group III [3, 4] were often tolerated. The use of only two "subgroups" for the larger periods is clearly inadequate. Experiment shows many cases in which well-known forms of the compounds of the elements exceed the highest typical forms of these groups, for example in the "copper subgroup" the forms of compounds R_2O_3 and even RO_2 [6] are well-known; in many of the rare-earths and thorite actinide metals, the forms of the compounds are considerably higher [7, 8], than in lanthanum and actinium, to the groups of which they are often referred. The question naturally arises concerning the distribution of all these elements in higher groups.

The situation set forth determined the goal of the present work and of the investigations of the author directed toward the solution of a number of problems of the systematic classification of the elements.

D. I. Mendeleev indicated that "true periodic law . . . as a law is purely chemical; based on our understanding of the atoms, joined in multiple ratios, discontinuously (and not continuously) and multiply . . . it has bearing above all on the form of the compounds. They are few, they are arithmetically simple and are repeated; their transitions are not continuous, and only a definite number of members is contained in each period" [9]. The overall series of the elements is, therefore, divided into periods, between those elements for which the maximum jump in the form of compounds has been established, i.e., between the halogens and the inert gases. Whereas in the table "Attempt at an Up-to-Date D. I. Mendeleev System of the Elements", just as for D. I. Mendeleev [2], the zero group begins the periods, it does not end them. Beginning with the second period, periods with an identical number of elements are repeated twice in the system.

The table shows that the third period doubles the second, the fifth doubles the fourth, and it must be asserted that the completed seventh period will repeat its composition and structure on a new base — on the new base of the sixth period.

This circumstance is registered by the introduction of the type. The prototype of the type was again indicated by D. I. Mendeleev, when he named the second and third periods "typical elements". Two periods of equal length are called a "type". In the system as a whole, as the table shows by differential hatching, there are four types, which distinctly convey the relationships of the similarities and differences of the elements. In this arrangement of the system, the second type of elements consists of the second and third periods, in each of which there are eight elements. They are all characteristic elements of the second type, the "typical" elements of D. I. Mendeleev, and have their direct analogs in all the subsequent periods of the third and fourth types.

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* The article was recommended for publication (in the nature of a discussion) by I. I. Chernyaev, director of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences, USSR.

The number of series and periods of the elements of this type from He to F and from Ne to Cl coincides, while the distribution in groups is as usual. The third type of elements consists of the fourth and fifth periods, in each of which there are 18 elements. Eight of these are analogs of the elements of the second type and have the s- and p-electron structure, from Ar to Ca and from Ga to Br in the fourth period, and from Kr to Sr and from In to I in the fifth. The other ten elements, in each of these periods consist of the characteristic elements of the third type; they have the d-electron atom structure. These are from Sc to Zn and from Y to Cd. The latter are distributed only in even series and as it were constitute a transition between those elements of groups II and III which are analogs of the second type, i.e., the transition from Ca to Ga and from Sr to In. As is well-known, the discrepancy of the elements in the groups of D. I. Mendeleev occurred only as regards their membership in the even and uneven series.

The inclusion of the ten characteristic elements of the third type in the transition from the s- to the p-electron atom structure is found in connection with the formation of the d-electron layer and has a more profound cause in the periodicity of the structure of the nucleus [10]. The fourth and fifth periods are each constructed of the two series, 4 and 5 and 6 and 7. The apportionment of the characteristic elements of the third type from Sc to Zn and from Y to Cd is shown in the table by horizontal hatching. They have their analogs in the periods of the fourth type. Thus, there is no need to use the vague "subgroups".

In addition, the introduction of the types restores the Mendeleevian distinction between the elements as regards even and uneven series, which is established by the mutual relation of elements not only in groups, but also in series. Thus, the characteristic elements of the second type from Al to Cl and their analogs in the periods of the third type from Ga to Br and from In to I, and also in the periods of the fourth type from Tl to At and from Etl to Eat are only found in the uneven series.

The fourth type of elements consists of the sixth and the still incomplete seventh periods. The sixth period includes 32 elements, which are distributed in four series: 8, 9, 10 and 11. The beginning and end of this period consists of the 8 elements which are analogs of the second type: from Xe to Ba begins the 8th series, while from Tl to At forms the 11th series; the 10 elements which are analogs of the third type: La and from Hf to Hg, which properly should be called lanthanoids, include elements with the d-electron atomic structure; the other 14 characteristic elements of the fourth type from Ce to Lu, or the serite metals of D. I. Mendeleev (rare-earths) are indicated in the table by vertical hatching. They are distributed in the 8th and 9th series, as by D. I. Mendeleev [2], which include the elements with an f-electron structure between those elements of groups III and IV which are analogs of the third type, i.e., between La and Hf.

Not only the electron structure, but also the data on the periodicity of the atomic nucleus [10] argue in favor of such a development of the periods of the fourth type in comparison with the periods of the second and third types.

The terms in the table show the beginning of the formation of the s-, p-, d- and f-electron shells of the atom, and coincide with the series which begin the new element types, which express the general correspondence between the electron structure of the atom and the structure of the system.

There is no doubt that the structure established for the sixth period occurs in the seventh period, since both of them belong to a single type. Thus Rn—Ra, are ahalogs of the elements of the second type and begin the 12th series, while 5 additional elements which are analogs of the second type from Etl to Eat should be distributed in the groups of the 15th series.

Actinium is an analog of the elements of the third type. The other 9 elements of this type from Ehf to Ehg should be found to occupy, in their properties, the indicated positions in the groups of the 14th series, and they, together with actinium, should properly be called actinoids. The series from thorium to centurium [Ct, element No. 100] consist of characteristic elements of the fourth type. These thorite [actinide] metals are distributed in the 12th and 13th series and, evidently, will be completed by three more synthetic elements of the same type: Etu, Eyb and Elu.

The first type represents a certain peculiarity in the system; of the elements it includes only hydrogen. The neutron, as regards charge and mass, could also be classified with the first type, as well as the positron and the neutrino. However, these intraatomic forms of matter, as well as mesons, the photon, the electron, etc., are not chemical elements, since they do not have isotopes and a number of the chemical properties of elements.

It is, therefore, impossible to compare the neutron with the inert gas group, and, consequently, hydrogen with the elements of groups I or VII. Hydrogen begins the system of elements. This circumstance was underlined in the structure of the system by its special position in the first descending group of the first type, period and series.

GROUPS		1	0	I	II	III	IV	V	VI	VII	8	7	6	5	4	SERIES	PERIODS	TYPES
	NUCLEAR CHARGE – GROUP COORDINATE → Z																	1
BEGINNING OF LEVEL 1 s-		1 H														1	1	
BEGINNING OF LEVEL 2 p-	MASS-SERIES COORDINATE		2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F						2	2	2
2			10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl						3	3	
BEGINNING OF LEVEL 3 d-			18 Ar	19 K	20 Ca	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	4	4	3
						31 Ga	32 Ge	33 As	34 Se	35 Br						5		
3			36 Kr	37 Rb	38 Sr	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	6	5	
						49 In	50 Sn	51 Sb	52 Te	53 I						7		
BEGINNING OF LEVEL 4 f-			54 Xe	55 Cs	56 Ba	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64			8	6	4
								Tb 65	Dy 66	Ho 67	Er 68	Tu 69	Yb 70	Lu 71		9		
							Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	10		
						81 Tl	82 Pb	83 Bi	84 Po	85 At						11		
4			86 Rn	87 Fr	88 Ra	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96			12	7	
								Bk 97 (Etb)	Cf 98 (Edy)	An 99 (Eho)	Ct 100 (Eer)	Etu 101	Eyb 102	Elu 103		13		
	↓ A						Ehf 104	Eta 105	Ew 106	Ere 107	Eos 108	Eir 109	Ept 110	Eau 111	Ehg 112	14		
						113 Etl	114 Epb	115 Ebi	116 Epo	117 Eat						15		
ELECTRON STRUCTURE TERMS		H_2O	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4	R_2O_7	RO_3	R_2O_5	RO_2	HIGHEST OXIDE FORMS		TYPICAL FORMS OF THE COMPOUNDS
		H_2	R	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH						HYDROGEN FORMS		

Attempt at an Up-to-Date Mendeleev System of the Elements

(Compiled by

A. I. Mashentsev,

1947-1950

Its peculiarity consits also in the fact that it does not have direct analogs in the periods of the subsequent types, while it manifests much in common with the most different elements, for example, with the halogens and with the alkali metals.

The table "Attempt at an Up-to-Date D. I. Mendeleev System of the Elements" manifests the same regularity that occurs within the periods, of the sequence of groups, i.e., the change in the valency limit (limiting the highest forms of the oxide and halogen compounds) in the transition from one element to the following proceeds successively by one unit.

In the periods of the second type, this change follows from 0 to 7. There is no basis for denying this sequence in the periods of the third and fourth types also.

Guided by this principle, in the eight group we have left only Fe and Ru – characteristic elements of the third type – and Os – their analog in the sixth period of the fourth type. After group VIII, a descending order of the sequence of changes in the limit of valency by one unit from Fe to Co, then to Ni, Cu and Zn, had to be allowed; the same was manifested in the 6th and 10th series of the fifth and sixth periods for the transitions of elements from Ru to Cd and from Os to Hg.

Mendeleev's note concerning the transition of the character of the elements of group VIII is reflected in the structure of the system by the fact that their arrangement together with the groups of copper and zinc proceeds in descending groups from 8 to 4. The latter are designated by arabic numerals in contrast to the usual (ascending) groups. The order of these groups provides for the sequential transition into the higher forms of compounds in elements of the various series, to wit: from Zn to Ga, from Cd to In and from Hg to Tl.

It is impossible to express the sequential changes in the valency limit between the elements of the beginning and end of the larger periods, by any other distribution of the transition elements in groups; this change is fixed by the forms of the compounds from groups 0 to VII.

In this sense, the period represents that part of the over-all series of elements, by extending which from one element to the following, manifests (or this must be expected) a sequential wave-like order of changes of the limit of highest valency by one unit. While it must be admitted that in the periods of the second type, the change in the valency limit of the elements has a monotonic course (one half-wave), in the periods of the third type it consists of three half-waves, and in the periods of the fourth type, seven half-waves. As is evident from the table, the change in the form of the hydrogen compounds also has a wave-like form.

The arrangement in accord with this principle of all the elements leads to the exclusion from group I of Cu, Ag and Au, and from group II of Zn, Cd and Hg; to the abolition of the triads of group VIII; to the liquidation of the "subgroups" and to the distribution of the rare-earths in the groups of the 8th and 9th series. All this, as is evident from the table, is not only occasioned by the aggregate of known properties [1, 9, 11-13], but is also in accord with the isotopic composition of these elements, i.e., with the distribution with respect to the mass and charge of the nucleus.

There are sufficient data on the correctness of the distribution of the rare-earths and thorite [actinide] metals in groups IV-VI [7, 8, 9, 14, 15]; as regards the distribution of the other groups, new experiments which will provide more precise data regarding this question, should be set up.

The distribution by groups is partially masked by the fact that in the even periods beginning each type, at the part of the characteristic elements, the higher forms rather regularly do not appear. Thus, with O and F in the second, from Fe to Zn in the fourth, from Il to Gd and from Ho to Lu in the sixth periods, only certain lower forms of the compounds are as yet known. In the uneven (doubled) periods of each type, the valency limits are considerably more completely manifested. This phenomenon also has bearing on the difference in the other elements of the even periods from those in the uneven periods in each type. Actually, almost all the elements of the even periods, in contrast to the uneven periods, are more difficultly oxidized, more difficultly form the highest forms of the compounds with oxygen and halogens, and on the other hand more readily form more stable compounds with hydrogen. Attempts have even been made to explain similar differences in the elements of the even and uneven periods by a special "secondary periodicity" [16]. However, such explanations do not harmonize with the Mendeleevian concept of the periodic law, which does not reduce to a simple repetition of the properties of the elements. For example, a comparison of the elements of group III shows that boron oxide is more readily reduced to the simple element that aluminum oxide. It is well-known, that the greater energy of the bond of aluminum with oxygen constitutes the basis for aluminothermy. On the other hand, boron hydrides are more stable than even the strongly polymerized aluminum hydrides. An analogous, but less pronounced relationship between the properties of Ga_2O_3 and In_2O_3 and also between the properties of Tl_2O_3 and Etl_2O_3, is to be expected. For thallium, as an element of an even period, the lower form of the oxide, Tl_2O is even more characteristic than Tl_2O_3.

The details in the periodicity of properties of the elements which have been registered occur throughout the entire system, and are naturally masked by the principal manifestation in the character of the elements, and sometimes their distribution in groups is even hampered to the extent that, other conditions being equal, the higher forms of the compounds are not observed. Actually, it does not follow from the fact that the most characteristic form of the oxide of thallium is Tl_2O and for lead, PbO, and not Tl_2O_3 and PbO_2, that the first should be classified as an alkali metal and the second as an alkaline earth metal.

All these considerations also apply to the elements of the descending groups. Difficultly in distributing the rare-earth and thorite [actinide] metals in the system is still caused by the established tradition of seeing only similarity between the elements in the groups and only difference in . the series. D. I. Mendeleev repeatedly emphasized [17] the necessity of studying the similarities and differences not only in the groups, but also in the horizontal series of the system. For the characteristic elements of the fourth type, this latter similarity even predominates. The order of transcribing the symbols of the elements and their number indicates that one must differentiate the relationship of similarity, manifested between the characteristic elements of a given type and their analogs, from the manifestations of more distant similarity between characteristic elements of different types.

Thus, the position of each element among all the others must be considered not only as regards membership in a group, but, obligatorily, also in its series, period and type. In the table "Attempt at an Up-to-Date D. I. Mendeleev Periodic System", there are 14 groups and 15 series, of which the three last series will consist of synthetic, radioactive elements. The physico-chemical properties of the approximately 20 elements which are as yet unsynthesized can be rather exactly predicted by their position in the groups and series of the end of the 7th period in type 4. The apportionment of the characteristic elements and their analogs among four types ought to facilitate the teaching of chemistry and the study of the periodic law, as well as its exposition in the literature.

The questions which arise in the system in connection with the introduction of the type, suggest the necessity of new experimental study of the highest possible forms of the compounds of many elements, a study which has already been partially begun [6, 18].

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ERRATA

In issues Nos 1-5 of the Journal of General Chemistry of the USSR, 1954, the following typographical errors occurred, and were repeated in the English translation:

Page	Line	Reads	Should read
22	Caption to Fig 1.	In all the thermograms, with the exception of the third, the upper transcription is the initial mixture and the lower transcription is for repeated heating, while in the third, the reverse is the case	In all the thermograms, with the exception of the tenth, the lower transcription is the initial mixture, the upper for repeated heating, while in the tenth, the reverse is the case.
35	Table 2 col. 1, heading	$[Bi^{+2}]$	$[Bi^{+3}]$
35	Table 3, col. 1, heading	$K_2C_4H_4O_2$	$K_2C_4H_4O_6$
40	Table 4, col. 1, heading	$Na_2C_4H_4O_5$	$Na_2C_4H_4O_6$
297	9, from top	diamine	diimine
459	13, from top	Acetaldehyde has been observed to form a compound $(H_2C{=}CHO)_2Hg{\cdot}HgO$ [8] and mercuric chloride in aqueous potassium solution	The formation of a compound $(H_2C{=}CHO)_2Hg{\cdot}HgO$ [8] from acetaldehyde and mercuric chloride in aqueous potash solution was observed.
567	Table 2, sample 2	n_D^{54} 1.4759; d_4^{54} 0.8508	n_D^{54} 1.4559; d_4^{54} 0.8408
596	Text, line 28 from top	The course of I and I_{III}	The course of I_{II} and I_{III}
657	Empirical formula, line 2 from bottom	$C_{15}H_{14}O_2N_2SCl$	$C_{15}H_{15}O_2N_2SCl$
657	Empirical formula, 3rd from bottom	$C_{15}H_{14}ON_2SCl$	$C_{15}H_{15}O_2N_2SCl$
662	line 6 from top	or a short chain	or a multiple chain....